Journal of Polymer Science: Part C, Polymer Symposia, No. 4

INTERNATIONAL SYMPOSIUM ON

Macromolecular Chemistry

Paris 1963

PART 3

Held under the auspices of the
International Union of Pure and Applied Chemistry
Paris, July 1-6, 1963

edited by *M. Magat*

Laboratoire de Chimie Physique de
la Faculte des Sciences de Paris, Paris, France

published by INTERSCIENCE PUBLISHERS a division of John Wiley & Sons, Inc.

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JOURNAL ON POLYMER SCIENCE, PART C, *Polymer Symposia*

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Published at irregular intervals by Interscience Publishers, a Division of John Wiley & Sons, Inc. Publication Office at 20th and Northampton Streets, Easton, Pennsylvania. Executive, Editorial, and Circulation Offices at 605 Third Avenue, New York, New York 10061. Subscription price, $225.00 per volume (including Part A: General Papers; and Part B: Polymer Letters). Foreign postage, $5.00 per volume (including Parts A and B).

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Sections on Polymerization in the Solid State, Polymerization under Unusual Conditions and with New Catalysts, and Electronic Properties of Natural and Synthetic Polymers appear in Part 2 of this Symposium.

GENERAL LECTURES

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1497–1509

Recent Results of Stereospecific Polymerization by Heterogeneous Catalysis

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Introduction

Results recently obtained at the Industrial Chemistry Institute of the Polytechnic of Milan on stereospecific polymerization will be briefly reported in this paper.

We shall restrict our attention to three principal topics, concerning particularly experimental results obtained from heterogeneous catalysis, by means of typical catalytic complexes containing titanium or vanadium, aluminum, and organometallic bonds. First, we shall deal with the activity and stereospecificity of catalysts prepared from $TiCl_3$ in the polymerization of propylene and of aliphatic olefins. Second, we shall deal with results concerning activity, stereospecificity, and mechanism of opening of the monomeric internal double bond of β-olefins and cycloolefins in their stereospecific copolymerization with ethylene. Finally we shall discuss a few results relative to the preparation of ditactic polymers of diolefins.

Activity and Stereospecificity of Catalysts from $TiCl_3$ and Organometallic Aluminum Compounds

It is well known that the reaction between $TiCl_3$ and an organometallic aluminum compound yields typical heterogeneous catalysts, which are stereospecific, at least for the whole class of the aliphatic α-olefins.[1]

By means of these catalysts we have been able to reach the highest stereospecificities so far obtained in the synthesis of isotactic polymers. Indeed, in some cases, stereospecificity can be considered as practically complete, because the resulting polymer must be considered as fully stereoregular, and such a polymer is the sole product of the reaction.[2,3]

It is further known that generally the conditions of a high isotactic stereospecificity are seldom secured in other numerous cases, in the literature dealing with the synthesis of isotactic polymers of different monomers.

The connection of the isotactic stereospecificity of catalysts from $TiCl_3$ with the nature and characteristics of the reagents used in the preparation of the catalysts, has been the object of our particular attention since discovery.

A few years ago it was pointed out that $TiCl_3$, by itself solid and crystalline, is polymorphous, and that this polymorphism has four crystalline modifications, called α, β, γ, and δ.[3-6]

The β modification, which is brown in color, all other conditions being the same, produced catalysts of limited stereospecificity for α-olefins. On the other hand, the other modifications, all of a violet coloration, are suitable for the production of catalysts of a high stereospecificity.[2]

This must be related to the structural peculiarities of the crystal lattice, which actually becomes the support of the catalytic active centers formed by $TiCl_3$, found on the surface of the particles and reacting with the organometallic aluminum compound.

In particular, the α, γ, and δ modifications differ in some structural characteristics due to different modes of packing of two-dimensional atomic layers in the three-dimensional lattice. These differences notwithstanding, it was found that the stereospecificity of the catalyst systems prepared from the above stated three modifications does not depend on the particular polymorphous modification in which $TiCl_3$ is found, but only on the nature of the organometallic reagent used in the preparation of the catalyst.[2,3]

From the structural point of view, it can be deduced that the stereospecificity is a result of the nature of the active centers situated on the surface of the particles at the point of emersion of single two-dimensional reticular layers whose characteristics are almost the same in the three crystalline modifications.

Interesting stereospecificity problems have been recently solved by a detailed study of the influence of the nature and the particular state of chemical activity of aluminum organometallic compounds on the activity and

TABLE I
Polymerization of Propylene with $TiCl_3$ (violet)–$AlEt_2X$ Catalysts[a]

X	Mean rate, g. polymer/hr. atm.-g. $TiCl_3$	Isotacticity index of the polymer, as wt.-% insoluble in *n*-heptane	Stability of $(AlEt_2X)_n$ to $(CH_3)_3N$
C_2H_5	33	83	Decomposed
F	10	83	"
Cl	11	93	"
Br	11	95	"
I	3	98	"
OC_6H_5	0	—	Stable
SC_6H_5	0.08	95	Decomposed
SeC_6H_5	0.4	94	"
NC_5H_{10}	0	—	Stable

[a] Polymerization conditions: $TiCl_3$ = 4 g./l.; Al/Ti = 1.5–2; p = 2000 mm. Hg; 70°C.; in toluene; 3 hr.

stereospecificity of the violet $TiCl_3$ catalyst, when used for the polymerization of propylene and of the first α-olefins of the normal aliphatic series.

Various organometallic compounds were prepared and then used in the preparation of the catalyst. These compounds were employed in the pure state and in some cases previously complexed with different substances, generally Lewis bases.

In a first set of runs several catalysts were prepared from $TiCl_3$ and organometallic compounds of the type reported in Table I, having the general formula Et_2AlX, where Et is the ethyl group and X may be either the ethyl group, a halogen, an alkoxy group, a similar group but with sulfur or selenium in the place of oxygen, or even a complex group containing nitrogen, such as piperidyl.[7]

The highest activities are found with catalysts prepared from triethyl aluminum and then diethylaluminum monohalides. Lower activities, and in some cases no reaction whatever, are consequent to the use of the other compounds of these series. In all cases, stereospecificity remains rather high, though markedly dependent on the nature of the organometallic compound used.

An interesting analysis of these results can be carried out by considering the reaction that the organometallic compounds above mentioned may singly give in the presence of Lewis bases. These compounds, when pure, are in part associated, to a state at least dimeric. In the presence of a Lewis base, if the base is sufficiently strong, the associated species may be dissociated, generating monomeric species complexed with the base in equilibrium with the free monomeric species.

The more active catalysts in Table I are those in which degree of association of the pure organometallic compound is lower than or equal to that of $Et_2AlSC_6H_5$ and which are dissociated by trimethylamine. This leads to the conclusion that the formation of the catalyst takes place only if there is in solution a sufficient concentration of the monomeric species of the organometallic compound and that therefore it is the last one that is responsible for the formation of the active centers on $TiCl_3$.

This conclusion agrees with previous observations, according to which certain catalysts, inactive at low temperature, become active when used or even only prepared at a higher temperature.[8]

The heat of dissociation of the organometallic compounds yielding active catalysts has been estimated as not exceeding 24,000 cal./Al atom.

In a second series of tests the activity and stereospecificity were studied by using systems derived from violet $TiCl_3$ and from $AlEt_3$ complexed with different Lewis bases in the molar ratio 1:1.[7]

Some significant results are to be found in Table II. The activities are high when the base is diethyl ether or triethylamine; these activities become vanishingly low with trimethylamine and pyridine. The heat of complexing of these bases with $AlEt_3$ increases in the following order: diethyl ether, triethylamine, trimethylamine, pyridine.

In this case also the 1:1 complexes, which supply active catalysts, must

TABLE II
Polymerization of Propylene with $TiCl_3$ (violet)–Base·$AlEt_3$ Catalysts[a]

Base	Mean rate, g. polymer/hr.-atm.-g. $TiCl_3$	Isotacticity index of the polymer, as wt.-% insoluble in *n*-heptane
$(C_2H_5)_2O$	8.5	84
$(C_2H_5)_3N$	8.0	85
$(CH_3)_3N$	0	—
Pyridine	0	—

[a] Polymerization conditions: $TiCl_3$ = 4 g./l.; Al/Ti = 1.5–2; p = 2000 mm. Hg; 70°C.; in toluene; 1 hr.

be dissociable by trimethylamine. Furthermore, the stereospecificity is not substantially different from that observed when noncomplexed $AlEt_3$ is used.

Once more these results are interpreted by supposing that it is the free monomeric species $AlEt_3$, in equilibrium with 1:1 complexes, that determine the activity and the stereospecificity of the catalyst.

The bases used could complex the $TiCl_3$ as well. This might lead one to think that, if this takes place, there might be a poisoning of the surface of $TiCl_3$, causing the inactivity of the system when strong bases are used. However, experiments in which the reagents are introduced in a different order show the organometallic compound to be preferred in the complexing.

These results have been confirmed by the study of catalysts from violet $TiCl_3$ and 1:1 complexes of Lewis bases with organometallic compounds of both an alkali metal and aluminum.[7]

Some activity and stereospecificity results are reported in Table III. It is particularly noteworthy that, whereas the activities are very low, the stereospecificities (when measurable) are the same as those typical of the violet $TiCl_3$ and $AlEt_3$ systems; that is, the stereospecificity is substantially independent of the complexing substances.

TABLE III
Polymerization of Propylene with $TiCl_3$ (violet)–(MeY·$AlEt_3$ + Base) Catalysts[a]

Organometallic compound	Polymer yield, g.	Isotacticity index of the polymer, %
$KCl·AlEt_3 + (C_2H_5)_2O$	14	82
$NaF·AlEt_3 + (C_2H_5)_2O$	Trace	—
$NaF·AlEt_3$ + pyridine	Trace	—
$NaF·AlEt_3 + (C_2H_5)_3N$	2	80
$KF·2AlEt_3 + (C_2H_5)_3N$	Trace	—

[a] Polymerization conditions: $TiCl_3$ = 1 g.; Al/Ti = 1.5–2; p = 2000 mm. Hg; 70°C.; in toluene; 12 hr.

TABLE IV
Polymerization of Propylene with $TiCl_3$ (violet)–Organometallic Compound Catalysts[a]

Organometallic Compound	Polymer, yield, g.	Isotacticity index, %
$Al_2Et_4Cl_2$	99	93
$Al_2Et_2Cl_4 + NC_5H_5$	20	92
$Al_2Et_2Cl_4 + (CH_3)_2NCHO$	15	92
$Al_2Et_2Cl_4 + [(CH_3)_2N]_3PO$	22	93
$Al_2Et_2Cl_4 + (C_2H_5)_3N$	8	93
$Al_2Et_2Cl_4 + (CH_3)_4NCl$	35	94
$Al_2Et_2Cl_4 + KCl$	40	93
$Al_2Et_2Br_4 + (n\text{-}C_4H_9)_4NBr$	18	95.5
$Al_2Et_2I_4 + (n\text{-}C_4H_9)_4NI$	20	98

[a] Polymerization conditions: $TiCl_3$ = 1 g.; Al/Ti = 1.5–2; p = 2000 mm. Hg; 70°C.; toluene; 3 hr.

Further interesting results, fully agreeing with those mentioned, have been obtained with the use of ethylaluminum dihalides complexed with Lewis bases or various substances together with violet $TiCl_3$.[2,7,9] Some of these results are indicated in Table IV. In particular, in the cases where the halogen is chlorine, stereospecificity is always the typical one of the system violet $TiCl_3$–Et_2AlCl. This may be attributed to the fact that two molecules of $EtAlCl_2$ are split and disproportionated by suitable bases in a complex with $AlCl_3$ and in a molecule of Et_2AlCl. Only this last would be responsible for the formation of the active centers, the former complex being sufficiently stable.

Even catalysts from analogous compounds or complexes containing bromine and iodine, instead of chlorine, have the stereospecificity typical of the system violet $TiCl_3$–diethyl-aluminum monobromide or monoiodide.[2,7]

The stereospecificities of these last catalysts are the highest reached so far in polymerizing propylene, butene-1, pentene-1, and other α-olefins. All the systems based on diethylaluminum monohalide are more stereospecific than the systems based on triethyl aluminum.

Reactivity, Stereospecificity, and Mechanism of Double Bond Opening in the Copolymerization with Ethylene of Olefins Having an Internal Double Bond

Since the first results were reported on stereospecific anionic polymerization it has been remarked that olefins with internal double bond are generally unable to give high molecular weight homopolymers, even with the most typical organometallic catalysts.

However, it was later found that copolymerization of these olefins was possible, provided the comonomer used was one, such as ethylene, having a small molecule and a double bond free of steric hindrances.[10–15] In such instances, the actual impossibility of these internal double bond olefins to be homopolymerized, makes it possible to obtain alternating copolymers, when working at high olefin/comonomer ratios.

Cyclopropene[16] and cyclobutene[17] are excluded, because they are capable of homopolymerization and give with ethylene random copolymers at any composition.

Following the concepts now outlined, it has recently been possible to prepare (e.g., with catalysts from vanadium salts and aluminum organometallic compounds) different copolymers with ethylene from *cis*-butene-2 and *trans*-butene-2,[10-12] pentene-2,[11] cyclopentene,[11,13] cyclohexene,[11,13] cycloheptene,[14] and *cis*-cyclooctene.[15]

In this type of reaction, cycloolefins are inserted in the chain by a simple opening of the double bond, and the enchained unit keeps the cyclic structure.

With regard to the reactivity of the cycloolefins in this copolymerization with ethylene, it has been observed that reactivity is clearly more marked in the cycloolefins having an odd number of ring carbon atoms. Furthermore, when with butene-2, the reactivity is markedly greater in the case of the monomer with *cis* configuration.

A series of systematic results[15] is summarized in Table V, in which one

TABLE V

Reactivity of Cycloolefins and of Butene-2 in their Copolymerization with Ethylene (Values Relative to Reactivity of Cyclohexene)

	Heterogeneous catalyst[a]		Homogeneous catalyst[b]	
Comonomer	p_{eth} = 50 Torr	p_{eth} = 100 Torr	p_{eth} = 50 Torr	p_{eth} = 100 Torr
Cyclopentene	4.8	8.7	8.4	12.4
Cyclohexene	1	1	1	1
Cycloheptene	3.1	5.2	8.4	12.9
Cyclooctene (*cis*)	0.45	0.67	3.3	4.1
Butene-2 (*cis*)	4.3	6.0	8.9	10.0
Butene-2 (*trans*)	1.3	2.2	1.6	1.5

[a] Polymerization conditions: 3.6 mmole VCl_4 + 9 mmole $Al(n\text{-}C_6H_{13})_3$ in 80 cm.³ heptane; 0.2 mole monomer; −30°C.; 7 hr.

[b] Polymerization conditions: 3.6 mmole V $(Acac)_3$ + 18 mmole $AlCl(C_2H_5)_2$ in 60 cm.³ toluene; 0.2 mole monomer; −30°C.; 7 hr.

can see the alternating values of the reactivities (here expressed as values relative to that of cyclohexene) in the complete series of the examined compounds.

Another important fact is that, particularly with cyclopentene, cycloheptene, and *cis*-butene-2, that is, with the more reactive monomers, alternating copolymers that are stereoregular and crystallizable were obtained and characterized.[18,19]

From the identity period and from the chain conformation in the ordered state, it has been ascertained by x-ray examinations, that the stereoregularity is due to an *erythro*-diisotactic arrangement.

Figure 1 indicates in Fischer's projection the structure of one of these chains.

With the remaining olefins studied, that is with those relatively less reactive, one has been so far unable to recognize crystallizable alternating copolymers.

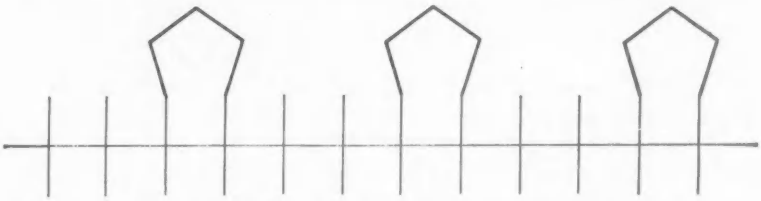


Fig. 1. *Erythro*-diisotactic structure (Fischer projection).

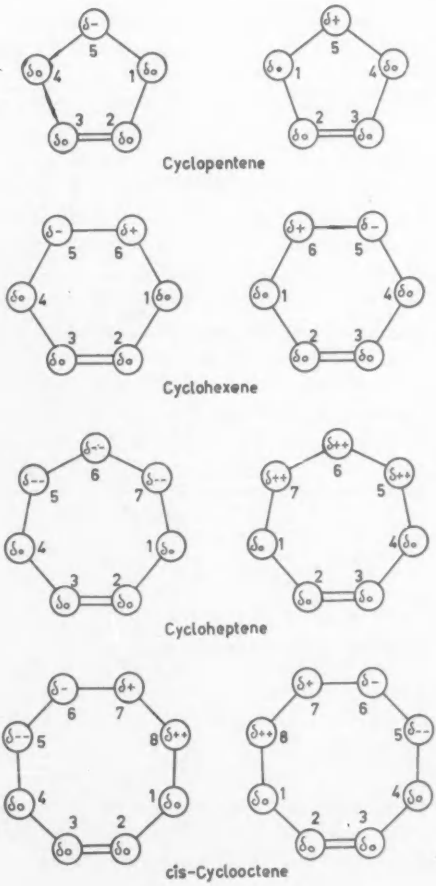
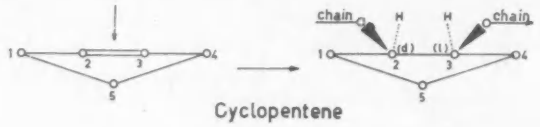


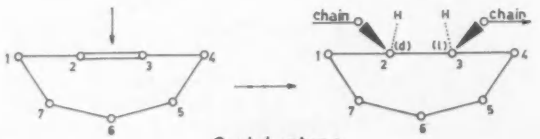
Figure 2.

Many considerations can be made on these results.[15] They can be essentially summarized as follows.

The thermodynamically most stable molecular conformations of the examined cycloolefins are schematically represented in Figure 2.



Cyclopentene



Cycloheptene

Figure 3.

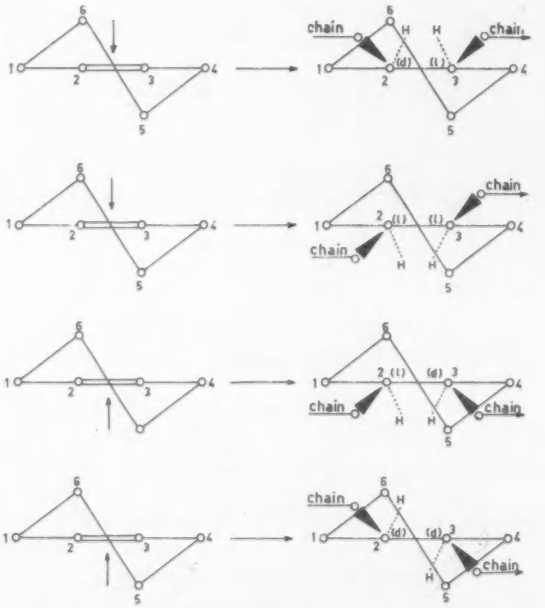


Figure 4.

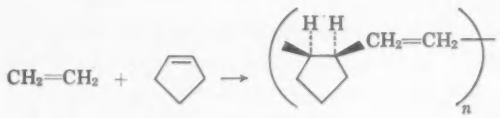
Each olefin is represented in the two ways in which it can be seen by an observer placing himself first on one, and then on the other side of a plane containing the four carbon atoms nearest the double bond (atoms from 1 to 4). The remaining ring carbon atoms are not on this plane, but on the one or on the other side of it. Their elevation is indicated in the figure by a plus or minus sign, for the atoms lying, respectively, on the side of the observer or on the opposite side.

One may see that the cycloolefins having an odd number of ring atoms (and they are the most reactive) show of a symmetry plane normal to the double bond. In these olefins the ring atoms, which do not lie in the reference plane, are all placed on the same side of it. This molecular geometry of cycloolefins having an odd number of ring atoms allows the free approach of an attacking reagent at one side of the double bond even if the reagent has a cumbersome size.

These considerations on reactivity might already justify the conclusion that the opening of the double bond in the above described coordination polymerization should be of the "*cis*" type, as schematically indicated in Figure 3 for the cycloolefins with an odd number of ring atoms.

The same opening mechanism cannot be considered favored in the case of cycloolefins with an even number of ring atoms. Here the situation can be seen in Figure 4.

Also the consideration of the stereospecificity leads in an unambiguous manner to the same conclusion, that is, the reaction, when stereospecific, takes place through a *cis* opening of the monomeric double bond. In fact, stereoregularity has been observed only in the case of (alternating) copolymers of cycloolefins having an odd number of ring atoms, and this stereoregularity is of the *erythro*-diisotactic type. This type of tacticity is the one immediately ensuing, even theoretically, when there are both a repetitive attack, with a constant geometric encounter, and the *cis* opening of the monomeric double bond. The situation is schematically represented for the case of cyclopentene as follows:



(1)

It is interesting to observe that the conclusion of a *cis* repetitive opening has already been reached in the preparation of diisotactic polymers of alkenyl ethers and β-chloro vinyl ethers by homogeneous catalysis.[20]

Actually, the behavior now considered of the reactivities of the olefins with internal double bond has been observed (as indicated in Table V), not only in the case of heterogeneous catalysts, but also in the case of corresponding homogeneous catalysts (e.g., vanadium acetylacetonate and diethylaluminum monochloride).

Thus the *cis*-type repetitive opening of the monomeric double bond appears to be a general fact in the coordination polymerization.

In relation to stereospecificity, there is a significant difference, however, between a heterogeneous and a homogeneous catalysis: whereas with cycloolefins (with an odd number of ring atoms) one obtains in all cases stereoregular alternating copolymers, with *cis*-butene-2 (more reactive than *trans*-butene-2) actually stereoregular alternating copolymers have been obtained exclusively by heterogeneous and not homogeneous catalysts.

This important fact shows that in the monomer coordination step, regulating the configuration of the entering monomeric unit, the ring structure of the cycloolefins has a helpful, promoting effect on stereospecificity. In other words, the ring plays a role analogous to that of conjugated double bonds or of atomic groups containing oxygen or nitrogen, typical of monomers with which only a stereospecific polymerization by positively homogeneous catalysis is at present possible.

On the contrary, *cis*-butene-2 has a behavior corresponding to that of normal olefins with a terminal double bond or of monomers having no other functional group of suitable electronic characteristics. In this case, in order to obtain a highly stereospecific synthesis, it is evidently necessary to have the surface action that is typified by the heterogeneous catalysis exclusively.

Polymerization of Diolefins

The stereospecific polymerization of diolefins presents aspects of greater complexity than that of monoolefins.

Diolefin polymers show of a greater number of stereoisomeric structures. In many cases, there are stereocenters of optical type together with stereocenters of geometric type, giving the possibility of essentially different tacticities. Furthermore the presence of two conjugated double bonds allows the application of either homogeneous or heterogeneous stereospecific catalysts, and in general the same catalysts with similar diolefins may give quite different results.

For various reasons, therefore, it is still difficult to formulate rules of a general character regarding the relationship between the stereoregularity of the polymer and the nature of the catalyst.

We would like, however, to report on a few interesting observations regarding stereospecific polymerization of 1,3-pentadiene. This monomer may give rise to four types of ditactic polymers having 1,4 enchainment: *trans*-isotactic, *trans*-syndiotactic, *cis*-isotactic, and *cis*-syndiotactic. Three of these have been prepared by us to a sufficiently high degree of steric purity.[21–24]

It is interesting to note that the *trans*-isotactic stereoisomer has been obtained so far only with heterogeneous catalysts, such as VCl_3 and AlR_3.[21] Similar catalysts, when made soluble (e.g. by formation of a complex of VCl_3 with tetrahydrofuran) produce, on the contrary, an amorphous

polymer, which seems to be stereoregular only with regard to the geometric isomerism, being atactic relative to the optical isomerism.[25]

Either *cis*-isotactic or *cis*-syndiotactic polymers have, on the other hand, been obtained by means of catalysts which are at least apparently homogeneous (titanium[23] or cobalt[22] acetylacetonates or alcoholates and organic aluminum compounds).

It is remarkable that the steric purity, and consequently the crystallinity, of the *cis*-isotactic polymer obtained by homogeneous catalysis is lower than that of the *trans*-isotactic polymer prepared by heterogeneous catalysis.

Somehow, this state of things calls to mind what has been observed in the case of 1,3-butadiene: practically total steric purity in *trans*-tactic polymers can be reached only by heterogeneous catalysis; conversely, the same practically total steric purity can be achieved in *cis*-tactic polymers only by suitable homogeneous catalysts.

Further experiments, however, now being carried out should clear up these relationships.

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Discussion

H. W. Coover (*Tennessee Eastman Co., Kingsport, Tenn., U.S.A.*): In this paper, the assumptions regarding the nature of the catalyst prepared with $EtAlCl_2$ are an oversimplification and do not explain the results which we obtained under carefully controlled conditions. Crystallinity fractionation studies, as well as closely controlled extraction studies with methyl isobutyl ketone, showed that the three-component catalyst consisting of violet $TiCl_3$, $EtAlCl_2$, and hexamethylphosphoric triamide produces polymers having fractions with higher stereoregularity and larger amounts of these fractions than the two-component catalyst consisting of Et_2AlCl and violet $TiCl_3$. In addition, infrared studies showed that benzene solutions of $EtAlCl_2$ and hexamethylphosphoric triamide, for example, contain none of the Et_2AlCl proposed here to explain the stereospecificity of the $EtAlCl_2$-type catalyst. While disproportionation reactions of alkylmetal halides are not uncommon, it should be noted that $EtAlCl_2$ forms stable complexes with many of the so-called Lewis bases referred to in this paper [e.g., see F. M. Peters, et al., *Can. J. Chem.*, **41**, 1051 (1963)]. Our kinetic studies indicated that the third component is not only necessary for the formation of the active site with the alkylaluminum dihalides, but that it must be associated with that site, since it influences both the rate and stereospecificity of the polymerization.

We would also disagree with the statement made in this paper that all systems based on diethylaluminum monohalides are more stereospecific than the systems based on triethylaluminum. We found the system based on Et_2AlF to be much less stereospecific than that based on Et_3Al.

F. Danusso: The stereospecificity of the catalytic systems based on $AlC_2H_5Cl_2$–hexamethylphosphoramide–violet $TiCl_3$, which were examined in our laboratories is not lower than that reported by Coover for the same systems; the same stereospecificity has been observed by us for the systems based on $Al(C_2H_5)_2Cl$–violet $TiCl_3$.

The formation of complexes between $AlC_2H_5Cl_2$ and Lewis bases is possible when the ratio is 1:1 (the paper by Peters quoted by Coover is concerned more precisely with the complexes with alkyl aluminum hydrides). The $AlC_2H_5Cl_2$–hexamethylphosphoramide mixtures in a 1:1 ratio and in the presence of $TiCl_3$, do not yield active systems for the polymerization of propylene as observed by Coover. The most active ternary systems are those prepared at a ratio of hexamethylphosphoramide to $AlC_2H_5Cl_2$ a little higher than 0.5; with this ratio it was demonstrated [see A. Zambelli, J. DiPietro, and G. Gatti, *J. Polymer Sci.*, **A1**, 403 (1963)] that $Al(C_2H_5)_2Cl$ is evolved, whereas addition complexes of the type (Lewis base)$\cdot[AlC_2H_5Cl_2]_2$ are not formed.

The results quoted by Coover dealing with infrared measurements are unknown to us and unpublished so far.

In contrast with what was observed by Coover, research done at our laboratories has shown that the stereospecificity of the binary systems prepared from $Al(C_2H_5)_2F$ and violet $TiCl_3$ is little different from that of the corresponding systems prepared from $Al(C_2H_5)_3$ for $t \cong 70°C.$ and a little higher for $t \cong 15°C.$ (see G. Natta, lecture held at the

2nd International Congress on Catalysis, Paris, 1960). Stereospecificity is markedly higher with corresponding catalysts containing Cl, Br, I instead of F.

We think that the lower stereospecificity observed by Coover for some catalytic systems based on $TiCl_3$ and dialkyl aluminum monohalides, with respect to that observed by us for the same systems, can be due to a different degree of purity of $TiCl_3$.

For further arguments concerning the behavior of catalytic systems based on monoalkyl aluminum dihalides–complexing substance–violet $TiCl_3$, see, in addition to the quoted papers, I. Pasquon, A. Zambelli, G. Gatti, *Makromol. Chem.*, **61**, 116 (1963), and G. Natta, A. Zambelli, I. Pasquon, G. Gatti, and D. DeLuca, *Makromol. Chem.*, in press.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1511–1528

Kinetics and Mechanism of Heterogeneous Stereospecific α-Olefin Polymerizations

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Introduction

Although developments in the use of organometallic complexes for the polymerization of olefins did not become widespread until recent years, work in this field is not new. Among the earliest references to such polymerizations is the work of Kraus,[1] who showed in 1940 that mixtures of inorganic halides and alkylaluminum halides were effective catalysts for the polymerization of olefins. As early as 1937, Hall and Nash[2] showed that mixtures of aluminum and aluminum chloride, when heated with ethylene, produced mixtures of alkylaluminum halides. In 1943, Fischer[3] applied for a patent that showed mixtures of aluminum, aluminum chloride, and titanium (IV) chloride to be effective catalysts for the low-pressure polymerization of ethylene. Since the conditions of Fischer's work were very similar to those used by Hall and Nash, it seems likely that some alkylation of the aluminum occurred to give organoaluminum compounds, which in combination with titanium (IV) chloride gave an active catalyst for the polymerization of ethylene.

In the meantime, independent work by Phillips Petroleum Company[4] and Standard Oil Company of Indiana[5] showed that oxides of molybdenum, chromium, and other transition elements, when in a partially reduced valence state and supported on a substrate, such as silica–alumina, could also be used to polymerize ethylene and propylene to solid crystalline polymers. The activity of such catalysts was increased by promoters, such as metals, metal hydrides, and metal alkyls, which led to the speculation that organometallic intermediates were involved in the actual catalyst sites.

Ziegler's[6] discovery of the low-pressure polymerization of ethylene using a complex catalyst made from alkylaluminum and titanium (IV) chloride created widespread interest and renewed activity in this field of catalytic polymerization. Since then, Natta[7] has published a series of papers elucidating the steroregulating effects obtained in the polymerization of propylene and higher olefins by use of what have been termed "Ziegler-type" catalysts.

As is natural in the field of complex catalyst chemistry, the exact nature of the catalyst and of the active catalyst site was not understood in the

early days, and the results obtained with even small variations in catalyst composition, valence state, etc., could not be predicted. As a result it was not possible to say with certainty which members of a relatively large class of related organometallic and transition metal compounds would show the desired catalytic activity. The situation was further complicated by the fact that some catalysts which were quite effective in forming high polymers from propylene and higher olefins gave polymers with widely different degrees of crystallinity, and this effect was also unpredictable. During these early days in the development of catalysts for olefin polymerization, a systematic study was initiated in Eastman laboratories to discover the factors controlling the stereoregularity of complex catalysts. The discovery of Eastman's three-component catalyst systems was the result of this work.[8] It was found that the addition of certain complexing agents to a mixture of an alkylaluminum dihalide and a titanium halide converted this inactive mixture to a highly active catalyst which yielded a product with the highest degree of crystallinity then known in propylene polymers. Only traces of amorphous polymers of propylene, which were formed in relatively large amounts with catalysts previously known, were present. The polymer, therefore, did not require extraction in order to remove amorphous material and gave a product of high stiffness and high tensile strength.

A considerable amount of information has been published by Natta and others on the kinetics and mechanism of the polymerization of olefins with Ziegler-type catalysts, but there is as yet little published material about complex three-component catalysts. The review of Bawn and Ledwith[9] presents an excellent summary of the present state of our knowledge. However, there is still considerable controversy over the actual nature of the active sites and their mode of action, and this may be expected to continue for some years to come.

In the present paper, I will discuss the experimental results we have obtained relating to the kinetics and mechanism of the polymerization of propylene with catalysts comprising mixtures of titanium (III) chloride ($TiCl_3$) with various metal alkyls and their complexes. On the basis of this work, a mechanism which we believe will explain most of the important experimental results obtained up to the present time using such catalysts is proposed.

Kinetics of Propylene Polymerization

With the apparatus shown in Figure 1, the rate of polymerization can be followed continuously throughout the polymerization by recording the pressure drop on the propylene reservoir. Rates obtained in this way correlate well with those obtained by direct methods, such as weighing the amount of polymer formed after a given time.

The three catalyst systems used for the kinetic studies were: system I, α-$TiCl_3$ + $(C_2H_5)_3Al$; system II, α-$TiCl_3$ + $(C_2H_5)_2AlCl$; system III, α-$TiCl_3$ + $C_2H_5AlCl_2$ + HPT (hexamethylphosphoric triamide). With

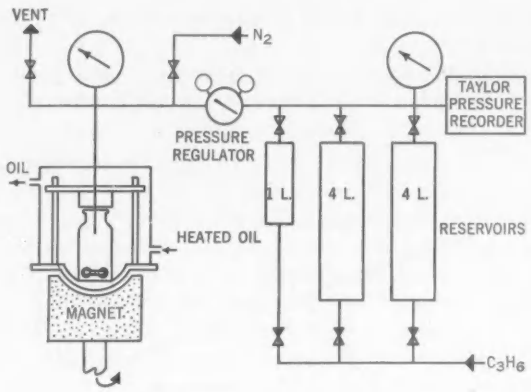


Fig. 1. Magnetically stirred kinetic apparatus.

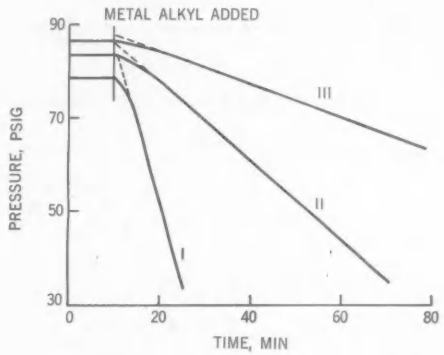


Fig. 2. Typical rate curves for catalyst systems I, II, and III.

these three systems, polymerization started as soon as the catalyst was contacted with the monomer. However, there was, as shown in Figure 2, an initial period of approximately 10 min. during which the rate accelerated continuously after addition of metal alkyl. After this the rate usually remained virtually constant for an hour or more. In Figure 3 are shown typical rate curves obtained from pressure-drop measurements and by gravimetric measurements. A single batch of $TiCl_3$ was used; it was divided into many small containers so that the activity remained constant over the period of the experiments. The rates recorded in most of this work are calculated from the straight-line portion of the curve. All experiments were run in duplicate, and the rates recorded are averages. If the duplicates disagreed by more than 20%, additional runs were made and averaged. Generally, the difference between duplicate experiments was less than 5%. For system II the overall polymerization rates per gram of $TiCl_3$

agree within a factor of two with those obtained by other workers under similar conditions.[7,10,11]

The standard catalyst ratio used for system III was 1.0/0.6/1.0 mole of $TiCl_3$/HPT/$C_2H_5AlCl_2$. With this system at 70°C., the overall rate of

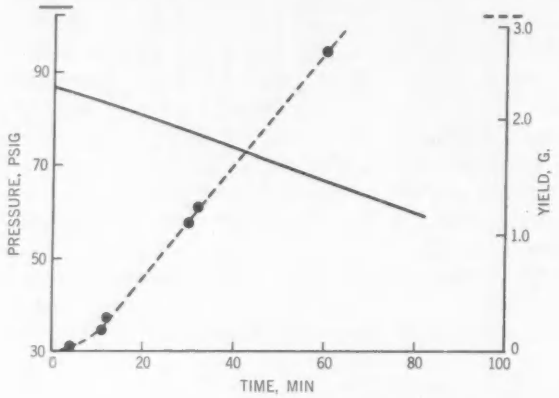


Fig. 3. Rate curves for catalyst system III.

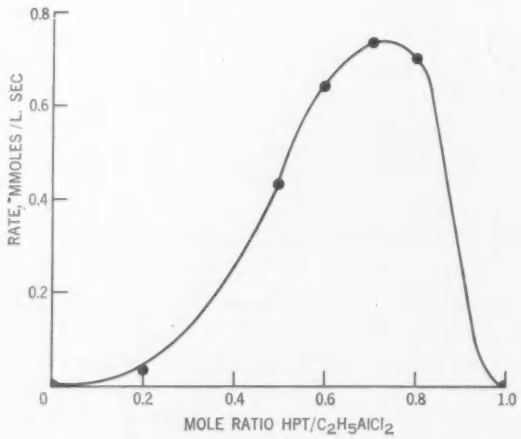


Fig. 4. Effect of HPT concentration on rate for catalyst system III.

polymerization, R_p, was a linear function of the pressure, and hence of the monomer concentration. The first-order dependence on monomer concentration has been shown for systems I and II by Natta and others.

The rate is also first-order in titanium concentration, as is also found for other $TiCl_3$ systems. Changing the amount of HPT, however, causes the rate to reach a maximum when the mole ratio of HPT is about 0.7 (see

Fig. 4). No appreciable polymerization is obtained in the absence of HPT or with more than 1.0 mole HPT per mole of $C_2H_5AlCl_2$. The rate of polymerization increases with temperature up to 80°C., with an apparent activation energy of 8.7 kcal./mole.

So far, the results we have obtained are consistent with those published on other catalyst systems containing $TiCl_3$. However, the key to understanding the fundamental or absolute mechanism of polymerization lies in obtaining a better knowledge of the nature of the active sites. In our work, tritiated methanol was used to kill the active sites, and an estimate of the number of metal–carbon bonds was made by counting the tritium chemically united with the polymer. The techniques used were similar to those of Feldman and Perry[12] and Kohn and co-workers.[10] It was shown experimentally that injection of 0.5 mole of methanol per mole of $C_2H_5AlCl_2$ was required to stop the polymerization completely. Smaller

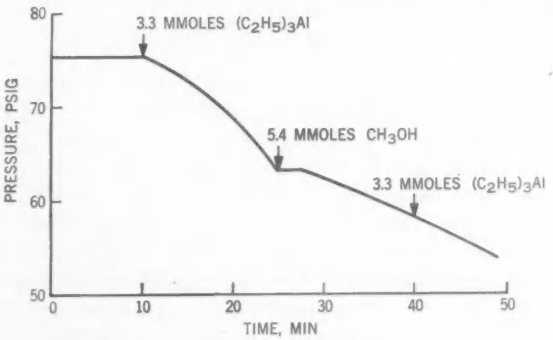


Fig. 5. Rate curves during catalyst deactivation with catalyst system I.

amounts would stop the polymerization temporarily, but after a few minutes it would start again, usually at a reduced rate. A typical rate curve for deactivation of system I is shown in Figure 5. This is strong evidence that the active sites are killed first, but some are regenerated if excess alkylaluminum remains in solution.

In agreement with the work of Kohn and co-workers,[10] our work indicates that the number of metal–polymer bonds increases rapidly with time, even when the rate of polymerization is constant. This indicates a relatively high rate of chain transfer resulting in the formation of a polymer–metal bond unattached to an active site. Measurements of the effect of propylene concentration on the rate of chain transfer indicate that the rate is directly proportional to the monomer concentration during the initial stages of the polymerization. This indicates that the chain transfer process involves both monomer and alkylaluminum and may be written:

$$Ti^* [X_2AlP] + AlX_3 + C_3H_6 \rightarrow Ti^* [X_3Al] + X_2Al(C_3H_6P) \quad (1)$$

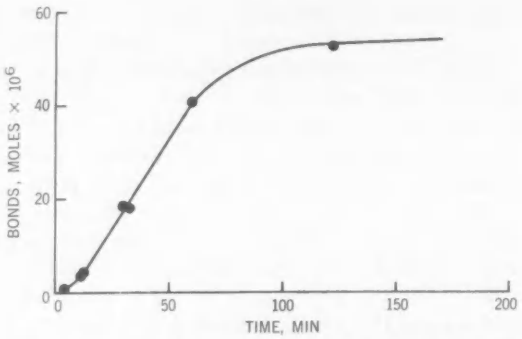


Fig. 6. Rate of metal–polymer bond formation in catalyst system III.

where X may be alkyl or halogen. The rate of chain transfer is then given by the expression:

$$R_{tr} = k_{tr} [\mathrm{M}] [\mathrm{A}] [\mathrm{C}^*] \tag{2}$$

where [M] is the monomer concentration, [A] is the concentration of metal alkyl, and [C*] is the concentration of active sites. Our studies indicate that the rate of chain transfer during the very early stages of the polymerization is very much higher than at later stages. This is shown in Figure 6 for catalyst system III and in Figure 7 for catalyst system II. This is in contrast to studies of Natta, Kohn, and co-workers, and Chien, who measured the rate of transfer at considerably higher conversions and found much lower values. Data abstracted from these papers are in Figure 8 along with our data plotted on a comparable scale. In our opinion, these results invalidate the extrapolations to zero time used by previous workers to estimate the number of active sites. An estimate of the number of active sites present during the early stages of the polymerization can be made, if one makes the reasonable assumption that the rate of chain transfer is proportional to the number of active sites as described in eq. (2). The total number of metal–polymer bonds formed by chain transfer in time t is as follows:

$$N' = \int_0^t R_{tr}\, dt = \int_0^t k_{tr} [\mathrm{M}] [\mathrm{A}] [\mathrm{C}^*]\, dt \tag{3}$$

The monomer concentration is constant under the experimental conditions, and [A] appears to be constant during the first 10–60 min. We can then write

$$N' = k_{tr} [\mathrm{M}] [\mathrm{A}] \int_0^t [\mathrm{C}^*]\, dt \tag{4}$$

The amount of polymer formed in time t is given by

$$w = \int_0^t R_p\, dt = k_p [\mathrm{M}] \int_0^t [\mathrm{C}^*]\, dt \tag{5}$$

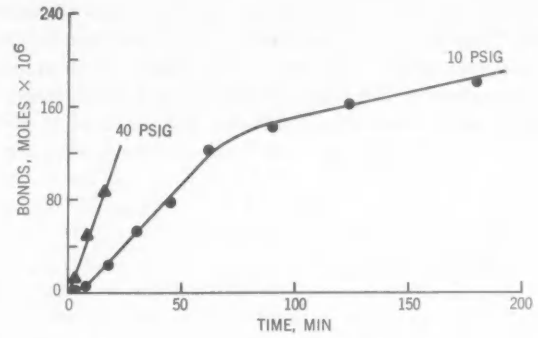


Fig. 7. Rate of metal–polymer bond formation in catalyst system II.

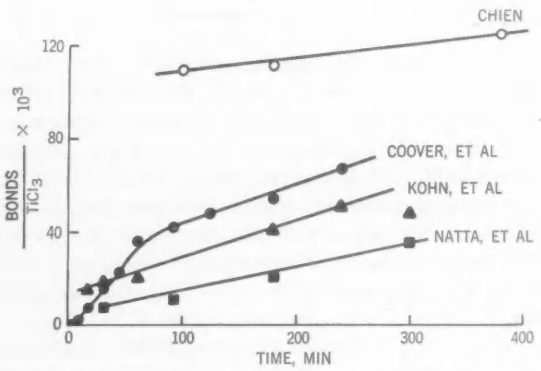


Fig. 8. Comparison of rate of metal–polymer bond formation in catalyst system II with that determined by other workers.

and

$$N' = w\,(k_{tr}\,[\mathrm{A}]/k_p) \tag{6}$$

The value of $k_{tr}\,[\mathrm{A}]/k_p$ can be determined from the ratio of the chain transfer rate, R_{tr}, to the polymerization rate, R_p, after steady-state conditions have been reached, at which time, presumably, the concentration of active centers is constant.

The measured number of metal–polymer bonds, N, at any time, t, will be equal to

$$N = [\mathrm{C}^*] + N' \tag{7}$$

which allows the calculation of $[\mathrm{C}^*]$ from the experimental data. If, as in the present case, the actual rate of polymerization at the time of killing is determined, it is then possible to estimate the absolute value of the propagation rate constant, k_p, from eq. (5).

The difficulty in such calculations is that the chain transfer rate is so much greater than was estimated from earlier work that it is necessary to kill the reaction at very low conversion (less than 0.1 g. polymer/g. $TiCl_3$); otherwise, the correction for chain transfer is very much larger than [C*], which must be determined by difference. Estimates of [C*] for catalyst systems II and III are shown in Table I along with values for the propaga-

TABLE I
Active Site Measurement

Catalyst system	$R_p \times 10^4$, moles/l.-sec.	$R_{tr} \times 10^7$, moles/l./sec.	[C*] $\times 10^5$, moles/l.	k_p, l./mole-sec.	τ, sec.	Active sites, moles/mole $TiCl_3$
I	22.6	26	~10	48	38	0.003
II	5.45	3.2	3	40	94	0.001
III	1.86	1.3	0.8	50	62	0.0002

tion rate contant at 70°C. The important factor to note is that the number of active sites per mole of titanium, estimated in this way, is far lower than estimated previously. This suggests that the active sites may be present only at dislocations of the crystal surface and are not available at virtually every part of the $TiCl_3$ surface as was indicated by earlier results. Further, the absolute propagation rate appears to be at least ten times greater than earlier estimates. This means that the lifetime of the growing polymer chain (between transfer steps) is very short (about 1 min.) at low conversions. The propagation rate is of the same magnitude as that for the free radical polymerization of styrene, for example: k_p = 145 l./mole-sec. at 60°C. for styrene. Our active center concentrations obtained with system II are compared with data reported by Natta, Chien, and Kohn and coworkers in Table II. The data were obtained with catalysts at similar

TABLE II
Summary of Active Site Data for Catalyst System II at 70°C.

Investigator	Method	Active sites, moles/mole $TiCl_3 \times 10^3$
Natta et al.[7]	C^{14}	6
Chien[11]	C^{14}	80–120
Kohn et al.[10]	H^3	28
Coover et al.	H^3	1

temperatures and monomer concentrations, and the measured polymerization rates were similar. We attribute these discrepancies to the measurement of transfer rates at relatively high conversions by the other authors. If our data at high conversion are extrapolated to zero time, the active center concentration is similar to that calculated by other authors.

It should also be noted that in our work, after about 60 min. in the case of system II catalyst, the rate of formation of metal–polymer bonds de-

creased markedly to about the value determined by previous workers (see Fig. 8). This occurs when the yield of polymer exceeds about 2 g./g. of $TiCl_3$. At this point the inherent viscosity of the polymer begins to increase and the distribution of molecular weights becomes considerably broader. We believe that this effect can be explained by the occlusion of the active site with relatively large amounts of polymer. This would reduce the rate at which the metal alkyl can reach the site and, hence, the effective rate of chain transfer. To explain the invariance of the polymerization rate, one must assume that the monomer is not prevented from reaching the site by the presence of polymer, at least not until considerably higher conversions are reached. Fractionation data indicate that the molecular weight distribution at very low conversions is relatively narrow and broadens rapidly with conversion due to the reduction in chain transfer rate by polymer occlusion.

Stereospecificity of Various Catalyst Systems

In studying a large number of catalyst systems, it is convenient to have an index which can be correlated with the stereospecificity of the catalyst. The most convenient measurement is a simple extraction with a refluxing solvent, such as 4-methyl-2-pentanone (methyl isobutyl ketone), which selectively dissolves the amorphous portion of the polymer. The relative amount of soluble polymer, a, expressed in per cent, is usually proportional to the degree of stereospecificity of the catalyst. A more convenient index $(100 - a)$ is defined as the "crystallinity index" of the polymer. In the past, such indexes have been used in describing the stereospecificity of catalyst systems, with the assumption that catalysts having large numbers of amorphous sites would also have lower stereospecificity at the crystalline sites. That this assumption is as least qualitatively correct is shown in Figure 9, where the percentage of stereoregularity for polypropylene fractions from various polymers is listed. It can readily be seen that the polymer made with catalyst system I, which has a crystallinity index of 63.8%, has a considerably lower degree of stereoregularity, even in the most crystalline portions of the polymer. Similar qualitative differences

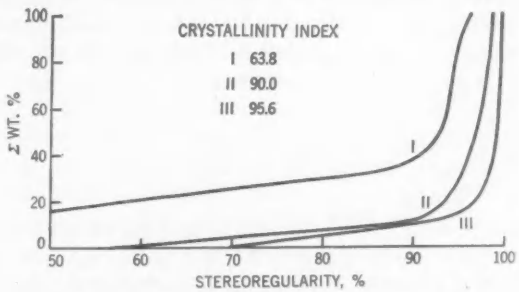


Fig. 9. Distribution of stereoregularity for polypropylene.

are shown between catalyst systems II and III, with the latter giving the highest degree of stereospecificity in the crystalline portion of the polymer.

In the discussion that follows, it will therefore be assumed that the crystallinity index, as defined above, will relate not only to the number of amorphous sites but also to the degree of stereospecificity of the crystalline sites.

In three-component catalysts like system III, both the stereospecificity and the activity of the catalyst are dependent on the ratio of the third component to $RAlX_2$; the maximum stereospecificity and rate are found at a mole ratio of 0.6–0.7.

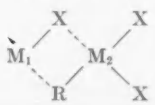
If the concentration of HPT/$RAlCl_2$ is kept constant, the stereospecificity decreases, but the rate increases as expected when the amount of $TiCl_3$ is increased. The crystallinity index of polypropylene made with catalyst system III increased slightly with conversion up to about 4 g. polymer/g. of catalyst and remained constant thereafter. The crystallinity index decreased slightly as the monomer concentration increased, or as the temperature increased. Molecular weight increased with increasing monomer concentration, but decreased as the temperature increased. This result indicates that the chain transfer processes responsible for molecular weight control have a higher activation energy than that of the propagation step. Preliminary estimates from viscosity determinations indicate an apparent activation energy of 8.7 kcal./mole for propagation and 14 kcal./mole for chain transfer.

Mechanism

The mechanism of heterogeneous stereospecific polymerization has been thoroughly discussed in a number of publications. Most authors agree that in one way or another the incoming monomer molecule must be preoriented. This orientation is imposed by local conditions whose geometric and energetic details are difficult to specify.

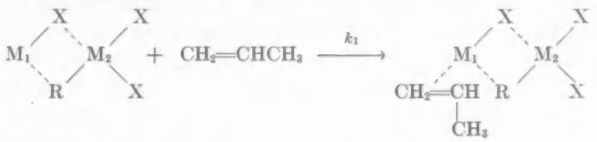
Based on the results of the present study, we propose a mechanism which admittedly draws heavily on the proposals of other authors, but which we feel provides a more adequate explanation of the observed facts.

It is postulated that the active catalyst is an electron deficient complex containing a transition metal and a highly electropositive organometallic compound similar to that suggested by Patat and Sinn.[13] The catalytic complexes have the following structure:



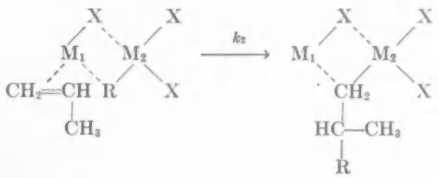
where M_1 is a transition metal, M_2 is the strongly electropositive metal of the organometallic compound, and R is the carbon from the latter. This active complex is probably formed at an imperfection in the crystalline lattice of the transition metal compound.

The driving force for the polymerization is the coordination of the olefinic π-electrons with the vacant *d*-orbitals of the transition metal.



(8)

This activated monomer then displaces the alkyl groups in the active site to initiate the growing polymer chain.



(9)

This type of mechanism leads to stereoregular polymer if each new monomer addition assumes the same orientation.

The geometry of a given active site and the associated metal alkyl dictate how effectively each new monomer addition at this site is compelled to assume a specific orientation. This will depend on the steric and polar factors imposed on the site by the atoms making up the site and its immediate environment.

The crystallinity of the transition metal compound will impart a steric orientation influence at the active site: the higher the crystallinity, the greater the steric orientation.

The stability of the active complex depends upon the electron affinity and the radius of the metal in the organometallic compound: the lower the electron affinity and the smaller the radius, the more stable the complex and the greater its steric orientation influence on the active site.

Stereoregular polymer chains have a strong tendency to assume a helicoidal configuration with a pitch which depends on the dimensions of the R group. The helices may show a right- or left-handed winding. It is reasonable to postulate that the growing polymer chain attached to the bridge carbons at a given site has a preferred orientation. In a growing helical chain, the last segment interacts not only with the preceding one but also with other segments located farther away along the chain. An activated monomer which undergoes addition to the growing helical chain will be preferentially oriented. Such an addition will be stereospecific if the rate of placement preserving the symmetry of the helix is much faster than the rate of any other placement. Thus, the growth of each new polymer chain at the bridgehead may proceed slowly until the chain length exceeds some minimum length and then it should become considerably faster. The rate of addition of even a single monomer having a different orientation should

be slower and should reduce the rate of addition for the next monomer (see Fig. 10).

If these conformational factors are operative, it suggests that a concerting influence of the last segment and of the corresponding segment in the preceding turn of the coil reduces the potential energy barrier of the propagation step. It further suggests that the copolymerization of two α-olefins having different polymer conformations or helical dimensions will tend to produce the corresponding homopolymers, a fact which has now been established in a number of systems. Conversely, random copolymers will be obtained only when catalysts of very low stereospecificity are used.

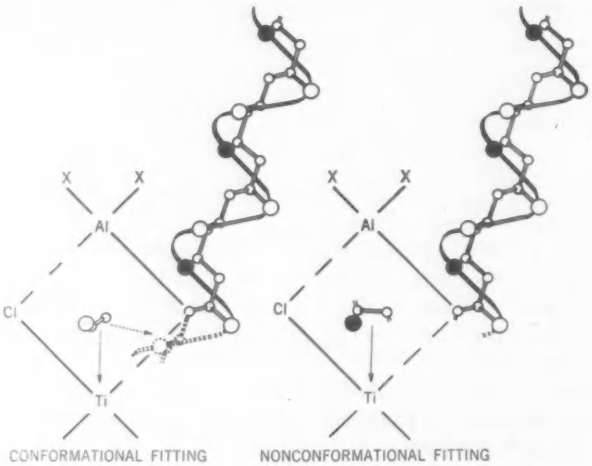
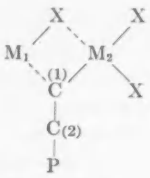


Fig. 10. Conformational fitting in active site.

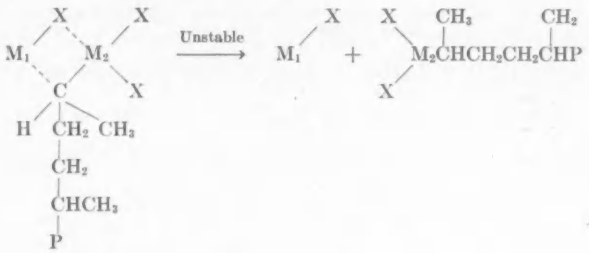
Catalyst systems having intermediate specificity will tend to produce stereoblock and segmented polymers. The observed rate of polymerization will depend on the number of active sites, the monomer concentration, and the absolute value of k_p.

The molecular weight and molecular weight distribution will depend on the ratio of termination and transfer rates to the propagation rate. The indicated transfer reaction is one in which the free organometallic compound displaces the organometallic compound associated with the active site along with the growing polymer chain and terminates the chain, leaving it attached to the metal M_2. The new complex starts a new chain. The frequency with which this happens should depend on concentration of metal alkyl and the stability of the catalyst complex. Our tritium results indicate that monomer is also involved in this process.

The stability of the catalyst complex will be greatly influenced by the nature of the bridgehead carbon (1) and the next carbon (2) in the chain.



A primary carbon (CH_2) at (1) and (2) gives the highest stability for a given complex. A CH_2 at (1) and CH-R at (2) is next in stability. A CHR structure at the bridgehead is unstable:



This type of reaction could possibly take place as a consequence of a propylene monomer entering the bridgehead backwards. The result is a transfer by monomer. That this speculation may have some validity is suggested by the known retardation of polymerization and reduction in molecular weight when internal olefins, such as 2-butene, are added to the polymerization. It could also be argued that the very high molecular weights obtained with ethylene using $TiCl_3/(C_2H_5)_2AlCl$ catalysts (system II) result because of the stability of the catalyst complex when the second carbon is unsubstituted. This concept of the stability of the bridge complex is also suggested by the observed relation between the stereospecificity of the catalyst and the molecular weight of the polymer produced. This is illustrated with catalysts I, II, and III in Table III, which show that an

TABLE III
Relationship of Stereospecificity with Molecular Weight

Catalyst system	Crystallinity index	$[\eta]$
I	63.8	1.77
II	90.0	2.50
III	95.6	3.20

increase in stereospecificity results in an increase in molecular weight.

We do not yet have sufficient data on active site concentrations with a large number of catalysts to establish whether the observed changes in rates of polymerization with different catalyst systems are due to changes in the number of active sites or in the absolute value of the propagation rate con-

stant, k_p. For this reason it is difficult to verify predictions relating to the effect of the structure of the catalytic complex on the absolute rate constant for propagation. However, this difficulty does not apply to the stereospecificity as measured by crystallinity index.

Based on the theoretical model described above, certain predictions can be made regarding the effects of various steric and polar factors at the site on the stereoregularity of the polymer. For example, if one alters the strength of the bridgehead carbon bond by substitution of various halides in the $(C_2H_5)_2AlX$ series, one would predict a weakening of the bridgehead Ti—C bond as the aluminum is made more electropositive. From Table IV, the observed stereospecificities of the catalysts support this prediction, being lowest for X = fluorine and highest for X = iodine. The addition of HPT to the $(C_2H_5)_2AlF$ catalyst causes a considerable reduction

TABLE IV

Effect of Catalyst Composition on Stereospecificity of $TiCl_3/(C_2H_5)_2AlX$/Third Component Catalyst System

(Monomer Pressure = 40 psig; Temperature = 70°C.)

X	Third component	Rate, mmoles/l.-sec.	Crystallinity index	$[\eta]$
F	None	1.89	36	1.34
F	HPT (0.4 mole ratio)	0.11	93	5.58
Cl	None	1.51	90	2.49
Br	None	0.98	93	2.80
I	None	0.73	96	2.60

TABLE V

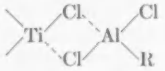
Effect of Catalyst Composition on Stereospecificity of $TiCl_3/RAlX_2$/Third Component Catalyst System

(Monomer Pressure = 40 psig; Temperature = 70°C.)

Crystalline form of $TiCl_3$	X	R	Third component: Mole ratio	Third component: Cpd.	Rate, mmoles/l.-sec.	Crystallinity index	$[\eta]$
α	Cl	C_2H_5	—	None	0	—	—
α	Cl	C_2H_5	0.6	HPT	0.68	96.4	3.14
β	Cl	C_2H_5	0.6	HPT	<0.09	75	3.72
α	Br	C_2H_5	0.6	HPT	0.53	98.3	3.14
α	I	C_2H_5	0.6	HPT	0.57	99.2	2.50
α	Cl	C_2H_5	0.7	$(C_4H_9)_3N$	0.93	95	3.06
α	Cl	C_2H_5	0.7	HPT	0.74	95	3.62
α	Cl	C_2H_5	0.7	$(C_4H_9)_3P$	0.73	97	3.11
α	Cl	C_2H_5	0.7	$(C_4H_9)_2O$	0.39	94	2.96
α	Cl	C_2H_5	0.7	$(C_4H_9)_2S$	0.15	97	3.16
α	Cl	CH_3	0.6	HPT	0.106	97	3.97
α	Cl	i-C_4H_9	0.6	HPT	0.085	95	3.85
α	Cl	C_8H_{17}	0.6	HPT	0.106	96	3.71

in rate, but a considerable increase in stereospecificity. A similar pronounced effect is shown in the dihalide/HPT system in Table V.

The function of the third component is apparently to complex with the alkylaluminum dichloride so that the active site can be formed through a carbon bridge. In the absence of a third component none of the alkylaluminum dihalides are active catalysts, probably because, in this case, the active site is tied up with a dimer structure of the following type:



The halogen bridge is formed to the exclusion of the alkyl bridge in the absence of a third component. As shown in Table V, the nature of the third component has only a minor effect on the stereospecificity of the catalyst, but the rate appears to increase as the compound increases in basicity.

It is well known that the nature of the R group in alkylaluminum compounds has a considerable effect on the stereoregularity of the polymer produced. This has been well established with trialkylaluminums (see Table VI). If, however, the alkylaluminum is not associated with the catalyst site (as it is in our mechanism) but is simply used to alkylate titanium, as in the mechanism proposed by Cossee[14] and others, then it is hard to see why the nature of the R group should have any effect, except on the first few monomer additions. In the alkylaluminum dichloride/HPT system, our mechanism would predict no effect of the alkyl group on the stereospecificity, since every alkyl group associated with a catalyst site would soon be on the end of a polymer chain and could have no lasting effect on the stereospecificity of the polymer. This is confirmed by the data in Table V, which show no effect on stereospecificity in changing from R = methyl to R = octyl. A maximum in rate is obtained with R = ethyl for reasons that are not immediately apparent, but which are possibly related to the ease of complex formation with the various alkyl dimers.

An increase in temperature would also be expected to reduce the stability of the bridge complex, and a successive decrease in stereospecificity with

TABLE VI

Effect of Alkyl Group in $TiCl_3/R_3Al$ Catalyst System on Stereoregularity of Polymer (Monomer Pressure = 10 psig; Temperature = 70°C.)

Crystalline form of $TiCl_3$	R	Rate, mmoles/l.-sec.	Crystallinity index	$\{\eta\}$
α	CH_3	1.17	59	0.78
α	C_2H_5	1.63	80	1.84
β	C_2H_5	0.90	48	1.12
α	C_6H_5	0.55	59	1.73

TABLE VII
Influence of Temperature on Catalyst System III
(Monomer Pressure = 40 psig.)

Temperature, °C.	Monomer concn., moles/l.	Rate, mmoles/l.-sec.	Crystallinity index	$\{\eta\}$
40	2.59	0.36	97.3	4.55
60	1.78	0.55	96.2	3.46
70	1.39	0.68	96.4	3.14
80	1.00	0.63	92.0	2.30

increasing temperature is shown for a typical three-component catalyst in Table VII.

As has been established by Natta,[7] the crystalline form of the $TiCl_3$ used affects both the rate and stereospecificity of the site (see also Table VI). A similar effect is shown in Table V with a three-component catalyst, although in this case the stereospecificities are both much higher; the rate with β form of $TiCl_3$ is very low indeed, indicating that there are very few sites available in the β form which are capable of forming highly stereospecific polymer.

Conclusions

In conclusion, our studies indicate that previous estimates of active site concentrations for $(C_2H_5)_2AlCl/TiCl_3$ catalysts are too high by at least a factor of 10. The reason for the previous high estimates is the marked reduction in chain transfer rate which occurs when the amount of polymer formed exceeds about 2 g./g. $TiCl_3$. It seems probable that this lower chain transfer rate can be attributed to the exhaustion of chemisorbed metal alkyl adjacent to the site and to the necessity for diffusion of free metal alkyl through a relatively thick layer of polymer to reach the site during the later stages of the polymerization. The chain transfer process appears to involve both alkylaluminum and monomer, but the effective monomer concentration is apparently not reduced by the diffusion process until a much later stage in the polymerization. The propagation rate is therefore unaffected, but the transfer rate is reduced, leading to the formation of polymer with much higher molecular weight. Extension of this process leads to the observed broad distribution of molecular weights in polypropylene.

As a result of the low value of active site concentrations (about 10^{-3} moles/mole $TiCl_3$) determined in this work, the absolute value calculated for the propagation rate constant for propylene polymerization is in the range of 50 l./mole-sec., and the average lifetime of a growing polymer molecule is about 1 min. at low conversion. These are of the same order as those for the free radical polymerization of styrene.

We believe that these results, particularly the active center studies, suggest that a re-evaluation of previous kinetic work should be undertaken.

In particular, more data should be obtained on the kinetics of the very early stages of the polymerization, and more attention should be directed to the role of the solid polymer layer which surrounds the active site. Kinetic studies of three-component catalyst systems indicate that the third component is not only necessary for formation of an active site with alkylaluminum dihalides, but it must be associated in some way with that site, since it influences both the rate and stereospecificity, even of the monohalide catalysts.

Our studies also indicate that the particular alkylaluminum used is associated with the active site, possibly in the form of a "bridge dimer" as proposed by Patat and Sinn, in order to explain the observed effect of changes in R of R_3Al on the stereospecificity of the catalyst. When only one R group is available, as in catalysts made from $RAlCl_2$, the R group does not remain at the site, but is attached to the end of the polymer chain and, hence, has no lasting effect on the stereospecificity of the site. The data also confirm that the alkylaluminum dihalide catalyst systems are different both in kinetics and stereospecificity from systems involving dialkylaluminum halides and hence cannot involve the same chemical species in the active sites.

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Discussion

M. G. Vaughan (*Dunlop Rubber Co., Birmingham, Great Britain*): Later in the conference, we shall present data obtained during analysis of the early stages of acceleration of heterogeneous polymerizations. We have established that the rates of polymerizations are dependent on the amount of polymer produced. The polymer itself causes considerable disruption of the catalyst particles and brings about large increases in the number of active sites by the generation of fresh catalyst surfaces. I should like to ask Dr. Coover whether such an effect could explain the results which he has ascribed to transfer reactions dependent on monomer concentration and alkyl concentration?

H. W. Coover: We found no evidence which would support this interpretation of our results. The rates were reproducible within 5% and showed no signs of the irregularity which would be expected if the catalyst surface was thus being disturbed. Also, since our rates were measured continuously and were constant after the first 10 min. for at least 1 hr. while the transfer rate was measured, the polymer produced does not influence the rate within this critical period.

M. A. D. Caunt (*I. C. I. Ltd., Herts, Great Britain*): What time interval elapses before the rate of production of polymer molecules falls markedly according to your data? Is the interval a matter of a few minutes or 1 hr? This matters, since with very reactive polymerization systems, such as those of practical industrial interest, it is very difficult to make reliable measurements of molecular weight by labeling polymer.

H. W. Coover: In these experiments, the rate of polymerization accelerated during the first 5–10 min., then remained constant for about 1 hr., after which the rate gradually decreased. At higher monomer concentrations, the initial period of acceleration is very short and usually is not observed, however, the decrease in rate occurs after a shorter time interval also. In the work reported in this paper, molecular weights were estimated from solution viscosity measurements and not by end group analysis.

The measured number of tritium end groups increases with time, both during the initial period of acceleration and during the period of constant rate of polymerization. We believe that it is fair to ascribe the acceleration in polymerization rate to an increase in the number of active sites, but it seems unlikely that this is occurring while the rate of polymerization is constant. The observed increase in tritium end groups must therefore be due to a chain-transfer process which forms a metal–polymer bond that is not capable of propagating the polymerization reaction.

P. Pino (*Pisa, Italy*): On what basis do you postulate a coordination number of 5 for the aluminum atom in the catalyst complex?

H. W. Coover: We do not pretend to know the exact structure of the coordination complex involved in the active site, although the coordination number of 5 used here for purposes of illustration is not unreasonable. For example, Peters and co-workers [*Can. J. Chem.*, **41**, 1051 (1963)], as well as many other investigations, have described aluminum compounds in which the aluminum shows a coordination number of 5.

M. Breslow (*Hercules Powder Co., Wilmington, Del., U.S.A.*): Why can't you explain the effects of the third component by a disproportionation of 2 $RAlCl_2 + B \rightarrow R_2AlCl + AlCl_3 \cdot B$? The type of differences you find are those to be expected from these heterogeneous systems, and it is dangerous to postulate new mechanisms on such evidence.

H. W. Coover: While disproportionation reactions of alkylmetal halides are not uncommon, it should be noted that $EtAlCl_2$ forms stable complexes with the complexing agents similar to those in question [F. M. Peters et al., *Can. J. Chem.*, **41**, 1051 (1963)]. We found that $EtAlCl_2$ and α-$TiCl_3$ in the presence of certain complexing agents, such as hexamethylphosphoric triamide, are active catalysts *per se*, and no Et_2AlCl was found to be present in these systems by infrared absorption analysis. The infrared spectrum of Et_2AlCl in benzene solution shows a characteristic absorption band at 18.3 μ. This band was absent in the infrared spectrum of benzene solutions of preheated mixtures of $EtAlCl_2$ and various complexing agents, and appeared in the spectrum of these mixtures only when Et_2AlCl had been added purposely.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1529–1549

Polymerisations Steréospecifiques en Milieu Homogène

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I. INTRODUCTION

En 1954, G. Natta obtint les premiers polymères vinyliques d'un degré élevé de stéréospécificité, cela au moyen des mélanges catalytiques organométalliques découverts par K. Ziegler. Après cinq ans,[1] de nombreux monomères étaient déjà polymérisés par l'effet des nouveaux promoteurs, et parmi eux, à côté des α-oléfines, également des diènes. Le nombre des systèmes promoteurs stéréospécifiques s'était aussi largement accru pendant le même laps de temps, comme on va le voir.

Les connaissances essentielles, dans ce nouveau domaine de la chimie macromoléculaire, sont dues surtout à Natta. C'est lui aussi, qui le premier développa des considérations théoriques sur le mécanisme de la polymérisation stéréospécifique. Les premiers résultats furent obtenus, avec des systèmes promoteurs solides; l'origine de leur activité était rapportée à l'orientation de la molécule de monomère à la surface du catalyseur solide, au moment oú elle s'intégre dans la chaîne polymère.[1] Cette hypothèse sur la nature hétérogène des réactions de polymérisation stéréospécifiques était plausible, et s'accordait avec l'expérience acquise sur les catalyseurs de Ziegler, et aussi avec les observations faites dans d'autres cas de polymérisation stéréospécifiques.[2,3]

Cependant, Patat et Sinn[4] déjà en 1958, sur la base de leurs réflexions à propos de la polymérisation des α-oléfines à basse pression, exprimèrent l'opinion que la polymérisation stéréospécifique devait être possible aussi en milieu homogène, à condition que la structure du catalyseur soit adéquate. De fait, en faveur de cette façon de voir, se présentaient déjà des observations plus anciennes de Schildknecht et de ses collaborateurs.[5] Dès 1947, ils avaient obtenu des polymères stéréoréguliers, un peu cristallins et relativement peu solubles, en provoquant la polymérisation des ethers vinyliques par la combinaison du fluorure de bore avec deux molécules d'ether. Leur comportement contrastait avec celui des poly-ethers vinyliques visqueux et amorphes, connus jusque là. Schildknecht rapporta les propriétés différentes de ses polymères à leur cristallinité, et proposa une disposition dans l'espace des motifs élémentaires, le long de la chaîne, que nous appelons aujourd'hui syndiotactique.[6] Staudinger[7] avait déjà obtenu

en 1932 des polyoxydes de propène cristallisés, et attribué leurs propriétés à l'agencement régulier des chaînes macromoléculaires.

Plus tard, Natta, au cours de ses recherches sur la polymérisation stéréospécifique, a repris la question de la structure des polyéthers vinyliques. A partir de leurs diagrammes de diffraction de rayons X, il a établi que les polymères de Schildknecht sont isotactiques. Mais plus important est le fait que la combinaison de fluorure de bore et d'éther, catalyseur puissant certainement cationique, ainsi que des mélanges catalytiques, tels que la dichlorure de dicyclopentadiényl-titane, peuvent provoquer des polymérisations stéréospécifiques et cela en milieu homogène. Alors, l'action orientante de la surface d'un catalyseur solide ne se manifeste pas.

Des découvertes analogues eurent lieu plus tard, en ce qui concerne la polymérisation du styrène et de l'isoprène, provoquées par le butyllithium. Enfin, il fut établi que, dans certaines conditions, la polymérisation par mécanisme de radicaux libres, en milieu homogène, ne fournissait pas toujours, elle aussi, des polymères atactiques. Dans beaucoup de cas, par exemple dans celui du mèthacrylate de méthyle ou du chlorure de vinyle, elle peut conduire à des polymères présentant une certaine stéréorégularité.

Ainsi, il est établi aujourd'hui, sans aucun doute, que la polymérisation stéréospécifique ne nécessite pas la présence d'une surface catalytique solide; son effet d'orientation sur la réaction de croissance de la chaîne n'est pas indispensable, et d'autres facteurs peuvent aussi entraîner la régularité stérique. De plus, la polymérisation stéréospécifique, en milieu homogène, n'est pas liée à un mécanisme particulier; elle peut s'effectuer aussi bien par voie ionique que radicalaire.

La revue qui suit à pour but de montrer quels sont les monomères les plus importants, qui jusqu'ici, peuvent se polymériser de façon stéréospécifique en milieu homogène, et quelles conclusions se dégagent, en ce qui concerne le processus réactionnel.

II. POLYMÉRISATION STÉRÉOSPÉCIFIQUE, EN MILIEU HOMOGENÈ, DES PRINCIPAUX MONOMÈRES

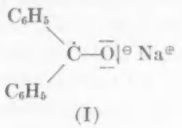
Les monomères polymérisables de façon stéréospécifique, en milieu homogène, se répartissent en plusieurs groupes. On a cru pendant longtemps que les α-oléfines simples, styrène inclus, n'étaient polymérisables, de façon stéréospécifique, qu'en milieu hétérogène. Cependant, rapidement des produits stéréoréguliers ont été obtenus à partir des diènes en milieu homogène. On connaît aussi des combinaisons non saturées simples, présentant un hétéroatome, c'est-à-dire des doublets d'électrons ne servant pas à des liaisons, qui sont polymérisables de façon stéréospécifique. A cette catégorie appartiennent non seulement les oxydes de vinyle et d'alcoyles, les *o*- et *p*-méthoxystyrène et la vinyl-2-pyridine, mais aussi les composés acryliques. Ces derniers sont en outre polymérisables de façon stéréospécifique, par mécanisme de radicaux libres, dans certaines circonstances. Il en est de méme du chlorure de vinyle.

1. Propène

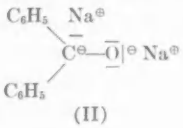
Natta avait insisté plusieurs fois sur la nécessité d'un système promoteur hétérogène, pour la polymérisation stéréospécifique des α-oléfines. Mais récemment, il a luimême signalé la polymérisation en milieu homogène du propène, en un polymère syndiotactique. Le catalyseur employé se forme à partir d'une combinaison de vanadium et d'halogénures d'alcoyl-aluminium.[8] Par exemple, un catalyseur actif à $-78°C$ en solution dans le toluène est obtenu en mélangeant le triacétylacétonate de vanadium, ou bien un complexe de tétrachlorure de vanadium et d'anisol, avec le chlorure d'aluminiumdiéthyle. Le rapport Al/V est un facteur essentiel; un rendement optimum et une haute cristallinité ne sont obtenus que pour des proportions moléculaires déterminées, lesquelles dépendent par ailleurs de la constitution du catalyseur. Les polypropènes syndiotactiques sont cristallisables; il est pratiquement impossible de séparer par extraction, des fractions de tacticités différentes. On ne sait rien sur le mécanisme de cette polymérisation, et sur la façon dont la stéréorégulation s'établit. A ce propos, on mentionnera la polymérisation du butadiène en 1-2, au moyen de promoteurs solubles.[9]

2. Styrène

La polymérisation stéréospécifique du styrène, au moyen des systèmes promoteurs hétérogènes de Ziegler-Natta,[10] des catalyseurs alfines[2] ou des métaux alcalins alcoyles,[3] est connue depuis longtemps. Une des premières observations sur la possibilité d'une polymérisation stéréospécifique homogène est du à S. Smith;[11] il utilisait comme promoteur le sodium-cétyle, dérivé de la benzophénone, et obtenait à 20°C, dans le toluène, un polystyrène cristallisable. Ce résultat est, toutefois, peu clair à divers points de vue; en particulier, plusieurs auteurs ont établi que la polymérisation du styrène n'est pas provoquée par le dérivé monosodé de la benzophénone (I), mais seulement par son dérivé disodé (II).[12, 13]



(I)



(II)

Tandis que I est soluble dans les liquides organiques aprotiques, tels que l'éther, le tétrahydrofurane ou le benzène, (II) est constitué par des particules rouges insolubles, qui cependant peuvent déclencher la polymérisation du styrène. Or, Smith indique que ses solutions promotrices ont été filtrées, au moins dans de nombreux cas; on doit donc supposer qu'elles étaient exemptes de sodium métallique et exemptes de la combinaison (II). Il est, de plus, étonnant que la polymérisation stéréospécifique ne soit possible que dans le toluène, ce qui suggère la formation de benzylsodium par action du métalcétyle sur le toluène.

La combinaison organo-métallique aurait alors fonctionné comme promoteur par l'effet d'une fraction hétérogène,échappant à l'observation de la solution bleue foncée.

L'aptitude des combinaisons organo-sodiques, telles que le benzyl-sodium, à provoquer la polymérisation stéréospécifique du styrène est connue.[14] Mais, à la température ordinaire, de petites quantités seulement de polystyrène eutactique se forment, àcôté de beaucoup d'atactique. Ceci est en accord avec les observations de Smith, qui pût faire cristalliser 10–35% du polymère (soit 1–12% du monomère employé).

Les recherches précédentes ne fournissent donc aucune preuve rigoureuse de la possibilité d'une polymérisation stéréospécifique du styrène.

En 1958, Sinn et ses collaborateurs[15] polymérisèrent le styrène, au moyen de combinaisons organiques du lithium. Ces recherches ne fournissent également aucune preuve certaine de la polymérisation stéréospécifique du styrène en milieu benzénique, car dans les conditions utilisées, ne se formaient que de très petites quantités d'un polystyrène cristallisant mal. La raison en était la température trop élevée, à laquelle s'effectuait la polymérisation, +5°C.

La première preuve indiscutable d'une polymérisation stéréospécifique, en milieu homogène d'hydrocarbure, au moyen du butyl-lithium, a été donnée par R. J. Kern,[16] qui, à −30°C et au dessous, obtint un polystyrène cristallisé. L'addition d'éther conduisait, même à −78°C, à la formation exclusive de polystyrène atactique.

De façon indépendante, nous avons fait les mêmes observations.[17]

Une conditions préalable à la polymérisation stéréospécifique, est l'emploi de *n*-butyllithium à peu près complétement exempt de chlorure de butyle. En outre, la température de polymérisation doit être suffisamment basse. Les polymères qui se forment en solution dans le benzène, au-dessus d'environ −25°C, sont près que complètement atactiques. En raison de la température de fusion du benzène, le polymère se trouve pendant la polymérisation, dans un état semi-solide. Après réchauffement à la température ordinaire, le mélange devient une solution complétement homogène. De même, on parvient à un polystyrène eutactique, lorsqu'on substitue le *n*-heptane au benzène. Toutefois, le système n'est pas alors strictement homogène, car le polymère formé est insoluble dans l'heptane.

La température convenable pour la polymérisation stéréospécifique dans l'heptane, va de −30 à −10°C, tandis qu'à −5°C, se forme seul le polystyrène atactique. Dans le toluène, utilisé comme solvant, le mélange, siège de la polymérisation, est encore complètement homogène à −30°C. Une partie du polymère formé est cristallisable et peut donc être considéré comme eutactique. Remarquable est le fait que les polymères eutactiques ne peuvent être obtenus, dans les conditions précédentes, qu'au moyen d'organo-lithiens dont les radicaux alcoyles sont linéaires, comme par exemple, les éthyl-, *n*-propyl-, *n*-butyl-ou *n*-amyllithium. Au contraire, les organolithiens ramifiés ne conduisent qu'à des polymères incristallisables.

On reviendra plus tard sur la signification de ces résultats, à l'occasion

de la discussion du mécanisme des polymérisations stéréospécifiques homogènes. Sur la cinétique de la polymérisation du styrène, provoquée par le *n*-butyllithium, existent de nombreuses recherches, qui la plupart, ont été conduites dans des conditions telles, qu'aucun polystyrène stéréorégulier ne se formait.[18–20]

Récemment Bywater et Worsfold[76] ont publiés qu'il n'est pas possible à gagner un polystyrène isotactique au moyen d'un butyllithium libre de l'hydroxyde de lithium. Mais en milieu pas complétement anhydre il se forme cet hydroxyde et une partie de polystyrène est isotactique et cristallisable. En ce cas la polymérisation du styrène au moyen du butyllithium n'est pas un exemple d'une polymérisation stéréospécifique homogène.

Enfin, on doit encore citer un travail de Friedländer et Thomas,[21] qui se rapporte à la formation de poly-α-*p*-diméthylstyrène cristallisable, provoquée par BF_3, BF_3 + ether, ou $SnCl_4$. Des polymères isotactiques doivent se former, mais en aucune manière un processus complétement homogène de polymérisation n'a pu être observé. Cela est vrai également dans le toluène ou le *p*-isopropyltoluène (cymène). Mais là aussi, des fractions cristallisables ont été extraites de la solution.

En dépit des expériences citées plus haut, dont la signification n'est pas encore tout-à-fait claire, la polymérisation anionique et stéréospécifique du styrène, en milieu homogène, doit être considérée comme un fait assuré.

3. Dièmes

La polymérisation de l'isoprène, sous l'influence de combinaisons métalliques solubles, est une des polymérisations stéréospécifiques homogènes les plus anciennes.[15] Au moyen des combinaisons organo-lithiennes, telles que l'éthyllithium ou le *n*-butyllithium, on obtient dans les solvants non polaires un produit très analogue au caoutchouc naturel, dont les motifs élémentaires possèdent, dans une proportion de 90%, la structure *cis*-1,4.[22] Egalement les combinaisons organo-magnésiennes, telles que les chlorure, bromure, iodure, de butylmagnésium, ainsi que le dibutylmagnésium, conduisent à une certaine régularité stérique, la structure 3,4 étant privilégiée.[23] Sur le mécanisme de la polymérisation des diènes, provoquée par les combinaisons organo-lithiens, se présentent diverses façons de voir.[22, 24] Il est établi sans contredit que dans le cas où la polymérisation est amorcée par le butyllithium, il s'agit d'une réaction en milieu homogène;[25] de même, au cours de la polymérisation en milieu hétérogène provoquée par le lithium métallique, se forment d'abord des composés organo-lithiens solubles, qui constituent les véritables initiateurs.[26] Ceci confirme, dans leur principe, les hypothèses originales de Stearn et Foreman,[22] qui donnaient comme première étape de l'action respective du lithium, et des organo-lithiens, les réactions:

$$2Li + CH_2{=}C(CH_3){-}CH{=}CH_2 \rightarrow Li{-}CH_2{-}C(CH_3){=}CH{-}CH_2{-}Li \quad (1)$$

$$LiR + CH_2{=}C(CH_3){-}CH{=}CH_2 \rightarrow R{-}CH_2{-}C(CH_3){=}CH{-}CH_2{-}Li \quad (2)$$

En conséquence, la vitesse de croissance est indépendante de la forme sous laquelle le lithium est utilisé, car c'est toujours le produit d'addition du lithium sur l'isoprène qui agit comme le véritable catalyseur.[26]

Des recherches cinétiques sur la polymérisation de l'isoprène, provoquée par le butyl-lithium, ont été effectuées par divers auteurs.[27–29, 32] Sinn et coll. trouvèrent une période d'induction vraie, dépendant de la concentration du butyllithium; ils écrivirent les réactions déterminant la vitesse de la façon suivante:[30]

$$^{m}LiC_4H_9 \xrightarrow[\text{Isoprène}]{k_a} {}^{m}Li[CH_2—CH=C(CH_3)—CH_2]_{n=1}—C_4H_9 \qquad (3)$$

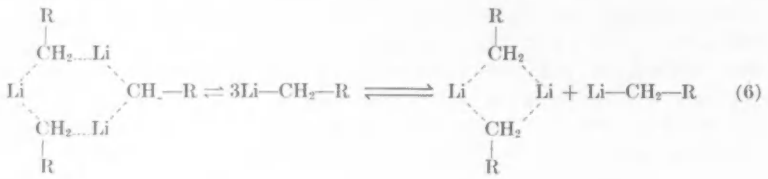
$$^{m}Li[CH_2—CH=C(CH_3)—CH_2]_n—C_4H_9 \xrightarrow[\text{Isoprène}]{k_w} {}^{m}Li[CH_2—CH=C(CH_3)—CH_2]_{n+1}—C_4H_9 \qquad (4)$$

La lettre ^{m}, placée en haut et à gauche d'un organo-lithien, signifie que celui-ci est sous la forme non associée, monomoléculaire. A ces réactions, se superpose un équilibre qui s'installe rapidement:

$$k\ {}^{m}\text{Li-Alcoyle} + l\ {}^{m}\text{Li-Alcényle} \rightleftharpoons (\text{Li-Alcoyle})_k(\text{Li-Alcényle})_l \qquad (5)$$

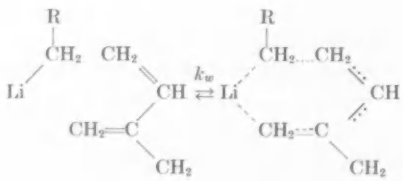
Le degré d'association $k + l$, pour une concentration de l'initiateur supérieur à 10^{-3} mol-g/l, est donné comme égal à 6. Pour une concentration plus faible, les degrés d'association plus bas jouent aussi un rôle. Sur la base des données cinétiques, Sinn et coll.[31] proposent les étapes suivantes.

Exemple d'un équilibre de dissociation:



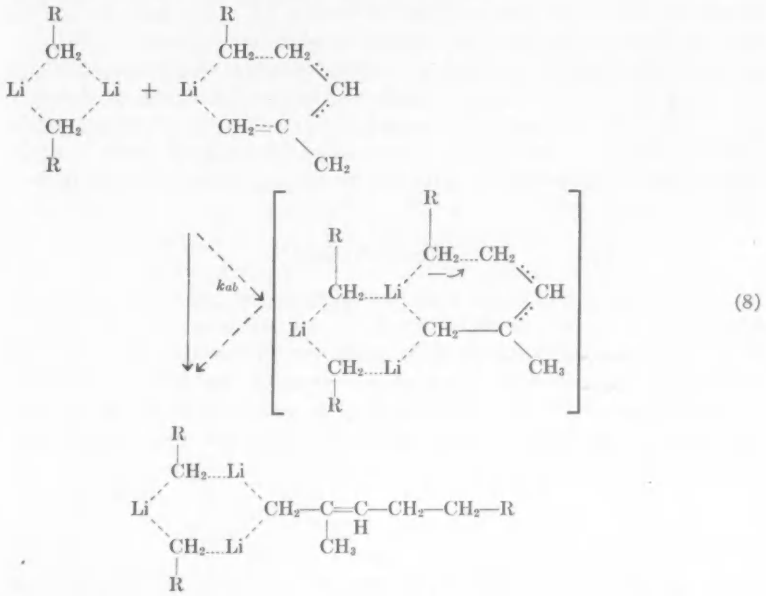
(6)

Activation:



(7)

Réaction de terminaison, écrite pour le dimère:



(8)

k_w est plus petit que k_{ab}, aussi la vitesse de la réaction (7) est-elle déterminante. En conséquence, il y a proportionnalité entre la vitesse globale de la réaction et la concentration des organo-lithiens non associés. Lorsque la dissociation des organo-lithiens croît, l'ordre de la réaction croît, en raison de l'association. Alors la réaction de terminaison (8) devient plus lente que l'activation représentée par (7) et détermine alors la vitesse.

Dans la première étape, le monomère forme une combinaison d'addition avec le catalyseur non associé, et dans celle-ci, sa configuration est bien déterminée. Au cours de la croissance, l' "insertion" d'une nouvelle molécule de monomère, se fait donc par l'intermédiaire de son produit d'addition avec l'organolithien, dans lequel il possède déjà la structure *cis* qui ne pourra plus changer.

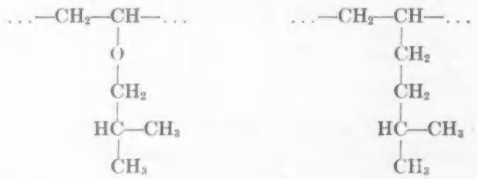
Quelques résultats principaux de Morton[75] sont d'accord avec cette hypothèse. Mais dans les hydrocarbures Morton suppose seulement des organolithiens dimères en équilibre avec le monomère. En outre il démontre qu'il existe dans le tétrahydrofuranne seulement des organolithiens monomères, solvatisés par le solvant.

Le pentadiène-1,3 peut également se polymériser en produit cristallisé stéréorégulier, sous l'action de catalyseurs agissant en milieu homogène. Ce sont des chlorures d'aluminiumalcoyle combinés à des dérivés de métaux du groupe de transition, par exemple du cobalt. De l'examen des spectres infra-rouge et de diffraction des rayons X, il a été conclu que la structure était syndiotactique *cis*-1,4.[34]

On doit citer également plusieurs recherches sur la polymérisation du butadiène, provoquée par les organo-lithiens.[35,36] Un type tout-à-fait différent de promoteur a été récemment employé pour provoquer la polymérisation du butadiène en émulsion, ainsi que dans l'éthanol ou la diméthylformamide.[37] Ce sont les hydrates du chlorure ou du nitrate de rhodium (III). Ils conduisent, avec un bon bon rendement, a un polybutadiène de structure *trans*-1,4 pour 90%. Aucune hypothèse n'a été émise, jusqu'à présent, sur le mécanisme de cette polymérisation stéréospécifique particulière.

4. Ether Vinylique

Comme il a été mentionnné dans l'introduction, les polyéthers vinyliques cristallisables, étudiés par Schildknecht et ses collaborateurs,[6] font partie des premiers polymères stéréoréguliers connus, bien que la nature précise de leur régularité fut élucidée plus tard, par Natta[38] et son école. Pour cela, il fallait déterminer la structure cristalline du polyoxyde de vinyle et d'isobutyle;[39] elle se révéla analogue à celle du polyméthyl-5-hexène-1 isotactique:



Schildknecht obtient un polyéther vinylique cristallisé eutactique, au moyen de l'éthérate de trifluorure de bore, c'est-à-dire d'un catalyseur cationique typique et puissant. Cette polymérisation se distingue de la plupart des polymérisations stéréospécifiques connues, non seulement par la nature du promoteur, mais aussi par le mécanisme de la polymérisation. L'éthérate du trifluorure de bore, n'est pas en état de provoquer la polymérisation stéréospécifique d'autres composés vinyliques.

En dehors de Schildknecht, Okamura et ses collaborateurs, entre autres, se sont intéressés plus tard à la polymérisation stéréospécifique des oxydes de vinyle et d'alcoyles provoquée par l'éthérate du trifluorure de bore.[40,41]

Selon la technique de polymérisation employée, la réaction peut se dérouler de façon homogène ou 'hétérogène." Si par exemple, on ajoute lentement et goutte à goutte l'éthérate de trifluorure de bore à une solution d'oxyde de vinyle et d'isobutyle dans un mélange d'hexane et de chloroforme, à −78°C, on observe une polymérisation dite hétérogène, ou cours de laquelle le polymère croît à partir de la surface des gouttes de catalyseur. Si au contraire, on verse le monomère dans le mélange du catalyseur et des solvants, alors la polymérisation a lieu en phase homogène, sans aucun indice d'une précipitation. Les cristallinités des deux polymères ainsi obtenus sont cependant absolument identiques, si bien que la polymérisation

hétérogène, dans ce cas, se distingue seulement par le fait que la vitesse de polymérisation sur les gouttes de catalyseurs est plus grande que la vitesse de dissolution du polymère formé. De toute façon, ces découvertes montrent que l'ordonnancement stérique des motifs élémentaires dans le polymère n'est pas lié à la nature hétérogène de la polymérisation. Plus récemment, la polymérisation cationique, en phase homogène, de l'oxyde de vinyle et de *n*-butyle a été décrite.[42]

Natta a ensuite montré dans un travail approfondi[38] que toute une série de catalyseurs de Friedel et Crafts modifiés, sont capables, comme l'éthérate du trifluorure de bore, de fournir des polyethers vinyliques isotactiques. Il entend par là des combinaisons halogénées des métaux, dans leur valence la plus élevée, une partie des atomes d'halogène étant remplacés par des groupes organiques tels que acétyle, alcoxyle ou acyle. Ces groupes doivent diminuer l'acidité du catalyseur, et en conséquence réduire la vitesse de polymérisation, car ici comme dans les autres cas, des vitesses de polymérisation trop élevées nuisent à la formation de polymères bien ordonnés stériquement. Cependant, l'activité cationique de ces combinaisons ne doit pas être complètement abolie par ces substitutions. Quelques exemples sont indiqués dans le Tableau I.

Au contraire jusqu'à présent, il n'était pas possible de provoquer la polymérisation stéréospécifique des éthers vinyliques au moyen des catalyseurs typiques de Ziegler-Natta, préparés à partir de trichlorure de titane et de triéthylaluminium, du moins dans la mesure ou le trichlorure de titane était exempt de tétrachlorure. Natta put cependant obtenir un polyéther vinylique cristallisé, en modifiant les systèmes promoteurs primitifs.[38] Une partie de ces promoteurs sont solubles dans le toluène; dans ce cas, la température de polymérisation présente une grande importance; au-

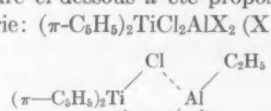
TABLEAU I

Polymérisation selon Natta[38] de l'Oxyde de Vinyle et d'Isobutyle au Moyen de Catalyseurs de Friedel et Crafts Modifiés, à −78°C[a]

Catalyseur	Solvant	Conversion, %	Propriétés des polymères
$Al(C_2H_5)_3$	Toluène	0	
$Al(C_2H_5)_2Cl$	"	85	Cristallins. Fraction insoluble dans l'acétone: 95%.
$Al(C_2H_5)Cl_2$	"	75	
$Al(C_2H_5)Cl_2$	*n*-Heptane	85	
$AlBr_3$	Toluène	70	Prédominance amorphe.
$TiCl_4$	"	70	Amorphe.
$TiCl_3CH_3$	"	65	Amorphe.
$TiCl_2(OC_3H_7)_2$	"	20	Cristallin. Fraction insoluble dans l'acétone: 90–95%.
$Ti(OC_3H_7)_4$	"	0	—
$TiCl_2(C_2H_5)_2$	"	0	—

[a] Dans toutes les experiences, 0,25 mol-g de monomère sont ajoutées lentement, en 3 h.; ensuite la polymérisation est poursuivie encore pendant 3 h. Proportions moléculaires monomère/catalyseur = 100.

dessus de $-30°C$, se forment exclusivement des produits amorphes. Des catalyseurs convenables, solubles dans le toluène, sont constitués, par exemple, de triéthylaluminium et de dichlorocyclopentadiényl-titane ou -vanadium. Ce sont là des complexes, dont toute une série a pu, entre temps, être isolée. La structure ci-dessous a été proposée par Natta pour une combinaison de cette série: $(\pi\text{-}C_5H_5)_2TiCl_2AlX_2$ (X = Cl ou C_2H_5).



De tels complexes sont solubles dans les hydrocarbures, et provoquent la polymérisation de l'éthylène. Cependant, les combinaisons $(\pi\text{—}C_5H_5)_2\text{-}TiCl_2AlCl_2$ et $(\pi\text{—}C_5H_5)_2TiCl_2AlClC_2H_5$, sont seules utilisables pour la polymérisation stéréospécifique des éthers vinyliques à basse température; alors en milieu homogène toluénique, il est possible de préparer un polyéther de vinyle et d'isobutyle cristallin. Natta attribue à ces catalyseurs un effet de polymérisation coordinative cationique.

A partir des faits mentionnés, qui se rapportent à la polymérisation des éthers vinyliques et des diènes,[8] Natta[38] conclue que les monomères, qui, outre la double liaison vinylique, contiennent encore une autre double liaison (diènes), ou un atome disposant d'une paire d'électrons π, ne nécessitent aucunement une surface catalytique solide, pour subir une polymérisation stéréospécifique même en solution, ils peuvent s'orienter, grâce à leur groupe fonctionnel. Les observations recueillies par divers auteurs s'accordent qualitativement avec le principe énoncé, concernant la structure des monomères.

5. Méthoxystyrènes

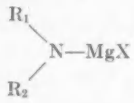
Parmi les monomères pouvant subir une polymérisation coordinative cationique selon Natta, figurent aussi les méthoxystyrènes.[44] Dans les éthers vinyliques et alcényliques, la liaison polymérisable est fixée directement à l'oxygène; il est intéressant de voir si malgré le fait qu'elle en soit très éloignée, séparée de lui par un noyau benzénique, la formation d'un polymère eutactique est encore possible.

Pour cela furent employés, comme pour la polymérisation des éthers vinyliques, les "catalyseurs de Friedel et Crafts modifiés." Tandis que des catalyseurs tels que $AlCl_2C_2H_5$, dans le toluène, ne provoquent pratiquement pas la polymérisation du *m*-méthoxystyrène, ils donnent avec les combinaisons *ortho* et *para*, des polymères amorphes; en tout cas, quelques uns des catalyseurs utilisables pour les éthers vinyliques étaient ici sans action. Les poly-*p*- et *o*-méthoxystyrène amorphes obtenus ne se distinguent pas par leurs propriétés des préparations obtenues par voie radicalaire; elles ne sont pas cristallisables. Par hydrogénation des polymères à 180°C, en présence de nickel Raney, il est cependant possible d'obtenir avec l'isomère *ortho* un produit, qui par ses propriétés et son diagramme de

rayons X, correspond au poly-méthoxy-2-vinyl-1-cyclohexane cristallisé. La structure de ce polymère n'est pas encore connue de façon certaine; c'est probablement un syndiotactique. On n'est pas parvenu jusqu'ici à hydrogéner le polymère de l'isomère *para*, cela pour des raisons non élucidées, si bien que, provisoirement, rien n'est connu sur sa régularité. En ce qui concerne l'isomère *ortho*, il est donc établi, de façon irrécusable, que sa polymérisation est possible en milieu homogène, bien que la distance entre le groupe vinyle et l'atome d'oxygène de l'èther soit ici plus grande que dans les éthers vinyliques.

6. Vinyl-2-pyridine

Natta et ses collaborateurs[45] déclanchèrent la polymérisation stéréospécifique de la vinyl-2-pyridine à la température a peu près de O à $-75°C$ et au moyen de divers promoteurs de la série:



ou, par exemple, $R_1 = R_2 = C_2H_5$, ou bien, R_1 = phényle, $R_2 = CH_3$; X = Cl ou Br. Le solvant est le toluène. Dans celui-ci le catalyseur lui-même est peu soluble, mais par addition de vinyl-2-pyridine, tout le dérivé métallique de l'amine se dissout. Cela montre que le monomère entre dans un complexe avec le catalyseur. Mais une solution claire, très étendue, de bromure de diéthyl-*N*-magnésium-amine dans le toluène, peut être employée comme promoteur; dans ce cas, la polymérisation stéréospécifique se déroule sans la présence d'une phase solide. Au contraire, avec le butyllithium, à de hauts degrés de conversion, se forme seulement un polymère amorphe incristallisable, tandis que le bromure de phénylmagnésium agit de façon stéréospécifique dans le toluène ou le chlorobenzène, mais ne provoque pas de polymérisation dans le *n*-heptane. Si la polymerisation est provoquée par le bromure de phénylmagnésium, des groupes phényles, décelables par spectroscopie infra-rouge, s'intègrent dans le polymère. On peut ainsi conclure à un mécanisme de polymérisation anionique: "... la polymérisation commence par l'insertion d'une molécule de monomère dans une liaison polarisée magnésium-carbone ou magnésium-azote."

Le pouvoir d'orientation manifesté lors de l'intégration d'une molécule de monomère dans la chaîne en croissance ramena Natta à la considération de la présence simultanée d'une double-liaison et d'un atome d'azote dans cette molécule. En présence de bases de Lewis, telles que l'éther éthylique, la stéréospécificité est fortement abaissée, ou même, comme avec la pyridine, complétement supprimée. Les bases s'opposent évidemment à la coordination du monomère sur la chaîne en croissance.

A partir de la vinyl-4-pyridine, on n'obtient, au contraire, que des polymères amorphes, ce qui est peut-être dû à la distance qui sépare l'atome

d'azote de la double-liaison; elle serait trop grande pour permettre la formation d'un complexe avec le catalyseur, qui parfois rendrait possible l'orientation du monomère sur la chaîne en cours de croissance.

7. Esters Acrylique et Méthacrylique

La préparation de polymères stéréoréguliers et partiellement cristallisables, à partir des esters acrylique et méthacrylique, au moyen de catalyseurs ioniques, a fait l'objet d'études approfondies. Tandis que la polymérisation a lieu selon le mode hétérogène,[46,47] lorsqu'elle est provoquée par le lithium métallique ou les composés alcoylés du sodium, du potassium, du rubidium et du caesium, on obtient au moyen des organo-lithiens, dans les solvants organiques à basse température, des polymères eutactiques au moins partiellement,[48] par une réaction en milieu homogène. Les composés de Grignard peuvent également conduire à des polymérisations stéréospécifiques.[49] Leur influence stéréorégulatrice sur la polymérisation radicalaire homogène du méthacrylate de méthyle a été observée dans des conditions déterminées.

Jusqu'ici les polymérisations stéréospécifiques des dérivés de l'acide acrylique ou de l'acide méthacrylique n'ont pas donné de produits purement isotactiques ou syndiotactiques, mais des chaînes présentant de fréquentes irrégularités. Par exemple, même dans un polyméthacrylate de méthyle largement isotactique, la longueur moyenne des séquences identiquement eutactiques est relativement petite, ce qui explique aussi la cristallinité la plupart du temps médiocre de ces préparations.[47] La résonance magnétique nucléaire[50,51] est une méthode sensible d'analyse de la configuration des polyméthacrylates de méthyle, qui a permis d'obtenir des renseignements relativement précis sur leur structure. De fait, les études effectuées sur ces préparations montrent qu'il s'agit presque toujours de copolymères à séquences eutactiques (stéréoblocs), mais ces dernières sont courtes.

Par polymérisation anionique du méthacrylate de méthyle dans un milieu polaire, tel que les éther-oxydes, se forment des polymères, dont les motifs élémentaires sont surtout liés de façon syndiotactique. Dans un solvant nonpolaire, comme le toluène, les liaisons s'établissent de préférence selon le mode isotactique.[47,52–54]

Des recherches cinétiques sur le processus de polymérisation du méthacrylate de méthyle à basse température ont été effectuées;[55] cependant, jusqu'ici on n'a émis aucune hypothèse claire sur le mécanisme. Sans doute, le mode d'addition du monomère à la chaîne en cours de croissance dépend de la solvatation par le solvant employé. On peut penser que les réflexions de Natta sur la polymérisation stéréospécifique des éthers vinyliques et de combinaisons semblables non saturées, possédant un hétéroatome sont applicables dans le cas des promoteurs solubles à la coordination et à l'arrangement stérique. Cette possiblité est due à la présence des groupes carboxyle et alcoxyle de la fonction ester.

La polymérisation radicalaire homogène[56] des dérivés des acides acrylique et méthacrylique donne des résultats analogues à ceux qui seront indiqués

dans le cas du chlorure de vinyle (cf. section II8). Les énergies d'activation des additions isotactique et syndiotactique diffèrent unpeu; il en résulte qu'à basse température, la disposition syndiotactique des motifs monomères du méthacrylate de méthyle se trouve favorisée (par exemple, en solution dans le toluène à $-40°C$, sous l'influence de la lumière ultraviolette activée par la benzoine). Lorsque la température croît, la préparation cristallise moins bien, car le nombre de liaisons isotactiques croît, augmentant les perturbations dans la structure des chaînes. Il s'agit donc ici d'une régulation stérique d'origine thermodynamique, qui se retrouve sous une forme semblable pour d'autres polymérisations radicalaires homogènes, conduisant à des chaînes principales portant des atomes de carbone asymétriques.

8. Chlorure de Vinyle

La polymérisation stéréospécifique du chlorure de vinyle manifeste, vis-à-vis de celle des α-oléfines, diverses complications. Tandis que l'on connaît beaucoup de polymères d' α-oléfines dont la disposition stérique eutactique est relativement uniforme, les chlorures de polyvinyle, comme les polyméthacrylates de méthyle, présentent tousles degrés in termédiaires, allant des polymères atactiques aux polymères largement ordonnés stériquement. Cela provient de ce que la plupart des catalyseurs dont l'efficacité sur la structure stérique est bonne, sont ici inutilisables, soit qu'ils ne provoquent aucune polymérisation, soit qu'ils réagissent sur le monomère.

Fordham,[57] en partant de considérations théoriques, a émis l'hypothèse que la réaction de croissance syndiotactique est favorisée, du point de vue énergétique, vis-à-vis de la réaction isotactique. La différence d'énergie potentielle correspondant à ces deux modes de croissance, ΔE, serait d'après ses calculs 1,5–2 kcal/mol. Cette prédiction a pu être confirmée expérimentalement.[58] Pour cela, on a préparé divers échantillons de chlorure de polyvinyle, à des températures allant de $-70°$ à $110°$, par voie radicalaire. La stéréorégularité a été déterminée au moyen des rayons X et infra-rouge. L'absorption infra-rouge, dans le domaine des fréquences d'élongation de la liaison C—Cl a été employée pour mesurer l'ordre stérique. C'est la bande située vers 635 cm^{-1} qui correspond à la configuration syndiotactique, et vers 692 cm^{-1} à la configuration isotactique des motifs élémentaires. Le rapport des absorptions, J_{635}/J_{652}, donne donc une mesure de l'importance relative des deux configurations dans les chaînes. En portant ces rapports en fonction de l'inverse de la température absolue, on obtient des points alignés, aux erreurs d'expérience près. La pente de la droite correspond à une différence d'énergie d'activation de 0,6 kcal/mol., entre les croissances isotactique et syndiotactique. Lorsque la température de polymérisation s'abaisse, la proportion des motifs élémentaires liés de façon syndiotactique croît, comme dans la polymérisation du méthacrylate de méthyle. Ces résultats viennent confirmer ce que la théorie prévoyait.

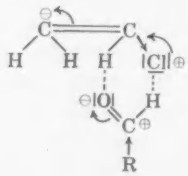
Plus tard, Gillespie et Burleigh[59,60] établirent que divers aldéhydes, utilisés comme solvants, présentaient une forte influence sur l'effet de régulation, dans la polymérisation radicalaire du chlorure de vinyle. Cette polymérisation provoquée par la décomposition thermique ou photochimique de l'azoisobutyronitrile, dans divers aldéhydes, conduit suivant la nature de ceux-ci et des autres conditions expérimentales à des polymères distincts, et quelquefois de haute cristallinité, caractérisables par les rapports d'intensité des bandes d'absorption infra-rouge. Les résultats les plus importants de ce travail se résument comme suit.

La polymérisation radicalaire, dans les benzaldéhydes substituées en para, est d'autant plus stéréorégulière que le caractère de donneur d'électrons du substituant est plus grand. Parmi les aldéhydes aliphatiques, de C_3 à C_{10}, l'action de l'aldéhyde *n*-butyrique est particulièrement grand. Mais les aldéhydes substitués en α par un groupe méthyle, tel que l'aldéhyde isobutyrique, donnent aussi des polymères très cristallins.

Dans l'aldéhyde butyrique, la température, entre -50 et $+50°C$, n'a que peu d'influence sur la nature eutactique et la viscosité des produits. En raison de la constante de transfert élevée des aldéhydes employés, leurs masses moléculaires sont relativement petites; en même temps, la vitesse de polymérisation est réduite.

Des recherches cinétiques sur la polymérisation du chlorure de vinyle, provoquée par l'azo-isobutyronitrile, dans le tétrahydrofurane, en présence d'acétaldéhyde, ont montré que la partie syndiotactique croissait en importance, lorsque la proportion d'acétaldéhyde augmentait. On s'est basé pour cela sur l'absorption infra-rouge. Les degrés moyens de polymérisation sont faibles[50–60] et les polymères contiennent, d'après les déterminations spectroscopiques, 1 à 2 groupes carbonyles par chaîne.[61]

Selon Razuvaev et coll.,[62] c'est le groupe aldéhyde qui est responsable de la polymérisation stéréospécifique du chlorure de vinyle. Les auteurs cités ont obtenu des polymères stéréoréguliers en provoquant la polymérisation par la lumière ultra-violette, en l'absence de promoteur et en utilisant des aldéhydes rigoureusement exempts de peroxydes. Ils supposent que le complexe entre l'aldéhyde et le chlorure de vinyle, qui est à l'origine de la régularité stérique s'écrit:



Il apparaît que la cristallinité du polymère est d'autant plus grande que la proportion moléculaire de l'aldéhyde au chlorure de vinyle est égale ou supérieure à 1:1. Mais lorsque ce rapport est inférieur à 1, des produits partiellement stéréoréguliers se forment encore. Dans des solvants, tels

que les cétones, les amides, les anhydrides d'acide, qui présentent un groupe $\diagdown C{=}O$, la formation de cycles semblables à 6 atomes, par addition, ne doit plus être possible, pour des raisons stériques ou énergétiques; il manque aussi, pour la réalisation de cette association, l'atome d'hydrogène du groupe aldéhyde.

III. HYPOTHÈSES SUR LE MÉCANISME DES POLYMÉRISATIONS STÉRÉOSPÉCIFIQUES EN MILIEU HOMOGÈNE

Les résultats exposés dans les sections précédentes ne sont pas tout-à-fait complets; ils permettent cependant quelques conclusions sur le mécanisme des polymérisations stéréospécifiques en milieu homogène. Tout d'abord, il est clair que de nombreux monomères sont susceptibles de subir une polymérisation stéréospécifique en milieu homogène, aussi bien par mécanisme ionique que radicalaire. Les principaux exemples sont rassemblés dans le Tableau II. On n'a tenu compte ici que des combinaisons dont il est traité dans la littérature; les brevets ont été laissés de côté. La répartition selon le mécanisme de la polymérisation, n'est possible que de façon grossière, car une distinction précise ne peut être faite jusqu'ici, dans tous les cas, entre une polymérisation ionique ressortissant soit au type de la formation de germe, soit au type de l'insertion, suivant Patat.[33]

Du Tableau II, on doit tirer la conclusion qu'il existe plusieurs sortes de régulations stérique possibles en milieu homogène, et en conséquence, qu'on ne peut s'attendre à l'énoncé d'un principe unique valable pour l'explication de ce processus.

Les circonstances les plus simples se présentent pour la polymérisation des dérivés de l'acide acrylique et du chlorure de vinyle. Là, on peut sup-

TABLEAU II
Monomères Polymérisables en Milieu Homogène, de Façon Stéréospécifique

Mécanisme	Monomères	Littérature
Cationique	Oxydes de vinyle et d'alcoyle	6, 38, 40, 41
	Oxydes d'alcényle et d'alcoyle	63
	o- (et *p*-) méthoxystyrène	44
	Vinyl-*N*-diphénylamine	74
Anionique	Propène	8
	Styrène	15–17
	Méthacrylate de méthyle	47, 52–54, 65
	Acrylate de méthyle	64
	Vinyl-2-pyridine	45
	Diènes	9, 15, 22, 30, 31 34
Radicalaire	Méthacrylate de méthyle	56
	Acrylate de méthyle	64
	Chlorure de vinyle	58–60

poser que des considérations thermodynamiques suffisent; elles reposent sur une légère différence énergétique entre l'intégration isotactique et l'intégration syndiotactique d'un motif. De façon corrélative, la régulation stérique est relativement faible, si bien que l'on ne doit pas compter sur la formation de produits eutactiques à un degré élevé, par un mécanisme de radicaux libres. La situation devient cependant différente, comme dans le cas de la polymérisation du chlorure de vinyle en présence d'aldéhydes, si une solvatation ou une association avec le solvant est possible. Celle-ci peut entraîner une orientation déterminée de la molécule de monomère qui s'intègre à la chaîne en cours de croissance. Peut-être doit-on expliquer aussi de cette façon la formation de produits cristallins, évidemment stéréoréguliers, qui prennent naissance par la polymérisation radicalaire des acétates de vinyle chloré ou fluoré. L'acétate de vinyle lui-même, dans les mêmes conditions, n'engendre que des polymères amorphes.[66] Rien de plus ne peut être dit à propos des polymérisations stéréospécifiques radicalaires, dans l'état actuel de nos connaissances. Il faudrait disposer pour cela de données expérimentales plus fournies, en particulier de connaissances plus précises concernant l'influence des divers solvants sur la structure des polymères formés.

Sans doute encore plus variées apparaissent les polymérisations réglées stériquement par un mécanisme ionique.[67] En ce qui concerne les polymérisations en milieu homogène, les faits établis par Natta sont significatifs; en dehors d'une double liaison dans la molécule de monomère, une seconde est nécessaire, ou bien un atome présentant un doublet d'électrons libre. (Une exception est cependant la polymérisation homogène du propène en un produit syndiotactique.)

Jusqu'ici, peu de systèmes ont donné lieu à des résultats expérimentaux clairs et solides, sur lesquels fonder le mécanisme de la réaction. Ainsi, dans le cas de l'isoprène, la formation d'un organo-lithien à partir du monomère est bien établie.[31] Dans le cas de la polymérisation du styrène, provoquée par le butyllithium, on ne peut décider entre une réaction initiale qui serait due à une association des molécules du promoteur, ou comme dans le cas de l'isoprène, aux molécules non associées de ce dernier. La question ne pourrait être tranchée que par des recherches cinétiques précises, alors on comprendrait peut-être aussi pourquoi seuls les organolithiens linéaires provoquent la polymérisation stéréospécifique du styrène, tandis que les promoteurs ramifiés ne donnent que des polystyrènes atactiques.[17]

Il est évident qu'il est nécessaire à contrôler le rôle d'un régulateur stérique par une phase hétérogène de l'hydroxyde de lithium.

En ce qui concerne la polymérisation stéréospécifique des éthers vinyliques, des auteurs japonais ont présenté une théorie faisant entrer en ligne de compte la géométrie de l'état de transition réalisé par le monomère, le polyion en cours de croissance et l'ion compensateur.[68] La plupart des théories de la formation de polymères stéréoréguliers en phase homogène développées jusqu'ici sont d'ailleurs simplement qualitatives.[69,70]

Une possibilité d'explication de la polymérisation stéréospécifique en

milieu homogène nous est fournie par l'hypothèse de Szwarc,[71] selon laquelle une configuration hélicoidale de la chaîne est nécessaire. Naturellement, une telle hélice se forme plus facilement dans les mauvais solvants que dans les bons, la solvatation par ces derniers étant plus forte. A l'appui de son hypothèse, Szwarc cite l'exemple, étudié par Williams et coll.,[72] de la polymérisation du styrène par le triphénylpotassium. Alors, du polystyrène eutactique se forme dans l'hexane, qui ne dissout pas le promoteur; au contraire dans le benzène, en phase homogène, seul du polystyrène atactique prend naissance. Williams explique le premier de ces faits par l'action orientale de la surface du catalyseur solide. Szwarc, au contraire, est d'avis que la surface solide du catalyseur ne joue ici aucun rôle; la formation de chaînes en hélice serait favorisée par la mauvaise qualité du solvant, en l'occurence l'hexane, pour le polystyrène. Cette hélice est naturellement plus stable aux basses températures, qu'aux températures élevées, ce qui pourrait expliquer les observations de Braun, Betz et Kern,[17] selon lesquels la formation de polystyrène isotactique provoquée par le butylithium, n'a lieu qu'à une température suffisamment basse. Cependant, la polymérisation du styrène par le *n*-amyl-lithium s'effectue, en milieu hétérogène, à $-40°C$, et fournit, aussi bien dans le toluène que dans le *n*-heptane, un polystyrène eutactique.[14]

Des considérations analogues sur la croissance en hélice du nitrile acrylique et du chlorure de vinyle ont été développées par Ham.[73]

En résumé, bien que de nombreux exemples de polymérisation stéréospécifique en milieu homogène soient aujourd'hui connus, une description quantitative précise du processus n'est possible que dans très peu de cas. Evidemment, les données expérimentales ne sont pas encore suffisantes. On doit cependant tenir pour certain, dès maintenant, que la grande diversité des résultats ne pourra être expliquée par un mécanisme unique de polymérisation.

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Discussion

F. Danusso (*Politecnico, Milan, Italy*): I have heard with much interest the review of Professor Kern. I should like to suggest a further useful element, which I think can be fundamental for a balanced comparison between homogeneous and heterogeneous stereospecific catalysts.

In practice, homogeneous catalysts can be differentiated into two types: catalysts acting stereospecifically at normal temperatures (rather few) and those acting at low temperatures (if in this case they are truly homogeneous). The first ones (e.g., soluble Ziegler-Natta catalysts in diene polymerizations) can lead to a full stereospecificity. The second ones in general produce only partially stereoregular polymers. Only the first ones can therefore be usefully compared with heterogeneous catalysts (e.g., the original Ziegler-Natta catalysts in olefin or diene polymerizations).

The second ones evidently reach a partial stereospecificity only by profiting by compromises between various factors (commonly differences in activation energies are invoked), and in principle cannot reach the same stereospecific efficiency as the first ones.

An example may be significant. Styrene can be polymerized by alkyls of Group I metals, and the polymers are said to be isotactic when prepared at low temperatures. However, these polymers have never been obtained fully isotactic, like polystyrenes prepared by heterogeneous Ziegler-Natta catalysis at normal temperatures (0–100°C. and more).

As evidence of this (F. Danusso, P. Ferruti, and I. Masini, unpublished data), we have prepared polystyrenes with butyl lithium at low temperatures, as reported in the literature. These polymers are practically insoluble in *n*-heptane (as are normal radical polystyrenes). They can show, however, some crystallinity. Accordingly, they do not dissolve completely on standing in methyl ethyl ketone, but leave a residue which is swollen, not "dry." In a preliminary fractionation, the molecular weight distribution of one of these samples appears to be a superimposition of two distributions, with markedly different average molecular weight, suggesting that at least two catalysts were effective in the polymerization. The first part of the distribution of lower molecular weight, is soluble in methyl ethyl ketone; the latter is not soluble, but swells. However, fully stereoregular polystyrene (so far prepared only by heterogeneous Ziegler-Natta catalysis) is completely insoluble (and does not swell) in methyl ethyl ketone (F. Danusso, and G. Moraglio, *J. Polymer Sci.*, in press), has a crystallinity reaching 40–50% [e.g., G. Natta and F. Danusso, Chim. Ind. (Milan), **40,** 445–50 (1958)] and melts at 240°C. (e.g., F. Danusso and G. Moraglio, *Makromol. Chem.*, in press.

W. Kern: The classification of initiators effective in homogeneous solution proposed by Professor Danusso appears to be quite efficient, although it differentiates more qualitatively, not quantitatively; the stereospecifically active Ziegler-Natta catalysts, soluble or insoluble, have a high but not complete regulating effect. We too have conducted fractionations of polystyrenes prepared with butyllithium, but we have no indication for the effect of two different catalysts.

Our stereospecific polystyrene prepared with *n*-amylsodium exhibits similar behavior to the polymer prepared with *n*-butyllithium. Here, too, fractionation yields portions with lower molecular weight and lower tacticity, the higher molecular weight fractions being well crystallizable and isotactic throughout.

Employment of methyl ethyl ketone as crystallizing medium for stereospecific polystyrene is not always unequivocal.

We have found that low molecular weight isotactic polystyrene is partially soluble, hence we prefer other liquids for crystallization [D. Braun, H. Hintz, and W. Kern, *Makromol. Chem.*, **65,** (1963)].

G. Smets (*University of Louvain, Belgium*): What is the degree of association of the organolithium compounds which are used for the polymerization of styrene, and what is the importance of it with respect to the rate of reaction and with respect to the structure of the polymer?

W. Kern: A degree of association for the organolithium compounds has not been determined; presumably there exists an equilibrium depending on concentration, as it is assumed by Sinn for the polymerization of isoprene. We thus cannot account for the influence of association on reaction rate and on the structure of the polymers obtained.

Probably the monomeric, not associated part of the organolithium initiators starts a "normal" anionic polymerization without stereoregularity, whereas an associated form (e.g., according to Patat and Sinn's general mechanism of stereospecific polymerization) responsible for tacticity.

In this way the formation of tactic and atactic polymers could be explained.

M. Breslow (*Hercules Powder Co., Wilmington, Del., U.S.A.*): It is my impression that the effect of aldehydes on the radical polymerization of vinyl chloride is to lower molecular weight, the lower molecular weight polymer being more crystalline. Do you agree?

W. Kern: This conception is probably correct and it is justified by the behavior of low molecular weight isotactic polystyrenes. Polyvinyl chlorides prepared in presence of aldehydes indeed have low molecular weights; but, on the other hand they also have more syndiotactic units than a polyvinyl chloride prepared radically at higher temperatures. This was confirmed by infrared and NMR investigations. Thus, the higher crystallinity may not only be attributed to the low molecular weight.

Dr. Rayner (*Great Britain*): I would like to support Dr. Breslow's remarks. Some years ago we studied vinyl chloride polymerization at room temperature in various sol-

vents. At first we too observed apparently more highly crystalline polymer (30–40% by X-rays) in certain solvents (e.g., ethers or esters) than normal (10–15%), but it soon became clear that the higher crystallinity correlated with a reduction in molecular weight. We confirmed this result by using HCl as a chain transfer agent for a vinyl chloride polymerization initiated by free radicals: the resulting low molecular weight polymer (intrinsic viscosity about 0.1) was also about 35% crystalline by x-ray examination.

W. Kern: To my knowledge there is no case of stereoregular polymer obtained by ionizing radiation in homogeneous phase at low temperatures. Suitable experiments certainly would be interesting.

H. B. van der Heyde: Ionizing radiations offer a means of initiating some polymerizations at low temperatures and under conditions where one can be sure of the homogeneity of the system. It would be interesting therefore to see whether by proper choice of monomer, solvent, and temperature one could obtain stereospecific polymers upon initiation with ionizing radiations, because in that case one would be relieved from the polar catalysts which often make the decision about homogeneity difficult.

Could Professor Kern offer me any information on whether attempts have been made along these lines and if so about the results?

L. Binder: We polymerized vinyl chloride in the absence of aldehydes at −60°C. with a trialkylboron initiator system. After fractionation we found that the stereoregularity of the fractions (measured by infrared spectra) increased with decreasing molecular weight.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1551–1570

Polymérisations en Phase Solide

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I. INTRODUCTION

Il y a cinq ans environ, on considérait encore comme des curiosités de laboratoire les résultats signalés par quelques auteurs selon lesquels la polymérisation de certains monomères pouvait avoir lieu en phase solide et on admettait généralement que ceux-ci constituaient des cas exceptionnels. Aujourd'hui, de nombreux monomères ont été polymèrisès à l'état solide, de très nombreuses publications traitent de ce sujet et plusieurs réalisations semi-industrielles permettent de penser que des techniques de ce genre pourraient, dans un avenir peut-être assez proche, servir à la production de polymères nouveaux dans des conditions intéressantes du point de vue économique.

Le mécanisme de la plupart de ces réactions est encore très mal connu et le chimiste cinéticien qui en aborde l'étude se trouve rapidement en face de problèmes appartenant à des disciplines souvent nouvelles pour lui, telles que la cristallographie ou la physique du solide. Or, lorsqu'il cherche à se familiariser avec ces techniques, il s'aperçoit que la structure cristalline et les propriétés des monomères organiques solides qui nous intéressent plus particulièrement ici n'ont été que très peu examinées jusqu'ici. Il en résulte des difficultés sérieuses lorsqu'on cherche à interpréter les résultats expérimentaux.

Dans une conférence faite il y a un peu plus d'un an sur ce même sujet, Magat[1] a passé en revue une cinquantaine de monomères dont plus de quarante avaient été polymérisés avec succès à l'état solide. Aujourd'hui, la liste de ces monomères est encore plus longue et il serait fastidieux de discuter ou même de mentionner la totalité des travaux parus à ce jour dans une conférence générale. Aussi nous bornerons-nous dans ce qui suit à analyser certains des facteurs qui régissent ce type de réaction en essayant de dégager quelques aspects communs aux différents systèmes examinés.

II. MODES D'AMORÇAGE DES POLYMÉRISATIONS EN PHASE SOLIDE

De nombreuses méthodes ont été utilisées pour amorcer la polymérisation des monomères solides. Certaines substances, comme le formaldéhyde

par exemple, se polymérisent "spontanément" lorsqu'on les congèle sous vide. Cette réaction semble être amorcée par des quantités infimes d'impuretés (eau?) à tel point qu'il est extrêmement difficile de conserver le formaldéhyde à basse température sans qu'il commence à se polymériser.

Kohlschutter et Sprenger[2] ont trouvé en 1932 que les vapeurs de formaldéhyde se polymérisaient au contact du trimère cristallisé (trioxane) en donnant un polyoxyméthylène fibreux qui était orienté selon l'un des axes cristallographiques du trioxane. Letort en 1933[3] et Travers en 1936[4] trouvaient que l'acétaldéhyde solide se polymérisait rapidement au moment de la fusion des cristaux de monomère. On sait aujourd'hui que cette réaction est amorcée par les traces d'acide peracétique qui se forment au cours de la photolyse, ou même spontanément au contact du monomère avec l'air.[5] En 1951, Schmitz et Lawton[6] ont signalé que différents monomères (en particulier le diméthacrylate de tétraéthylèneglycol) se polymérisaient à l'état solide après irradiation avec des électrons accélérés à très basse température. A partir de 1954, la polymérisation radiochimique de l'amide acrylique cristallinea été décrite par deux groupes de chercheurs;[7,8] cette réaction était amorcée par des rayons gamme à la température ordinaire. Depuis cette date, de nombreux monomères ont été polymérisés à l'aide des radiations ionisantes et aujourd'hui le procédé radiochimique tend à devenir le mode d'amorçage "classique" dans ce domaine. Les études ont porté sur la plupart des monomères vinyliques usuels ainsi que sur des composés hétérocycliques ou encore sur des monomères particuliers qui n'ont pas été polymérisés jusqu'ici avec des méthodes d'amorçage conventionnelles ou qui ne se polymérisent que très difficilement. Des listes des monomères qui ont été ainsi polymérisés avec succès existent dans la littérature.[1,9,10]

A côté de ces études radiochimiques, des polymérisations ont également été amorcées à l'état solide avec des initiateurs radicalaires dispersés dans les cristaux de monomère[11] ou encore avec des catalyseurs ioniques qui diffusaient progressivement à l'intérieur des cristaux.[12–14]

D'autres études récentes ont porté sur la polymérisation photochimique des acides acrylique et méthacrylique cristallisés renfermant ou non un sensibilisateur,[15,16] sur la polymérisation thermique des *p*-acétamido et *p*-benzamidostyrene[17,18] ainsi que sur l'amorçage de la polymérisation de certains monomères solides par des décharges électriques[15] ou par des chocs mécaniques.[19] Ce dernier procédé a été utilisé en particulier dans le cas du trioxane. Des phénomènes de triboluminescence ont été mis en évidence et les cristaux de monomère ainsi traités subissaient une "post-polymérisation" analogue à celle qui est observée après irradiation des cristaux de ce monomère.[19] Une technique intéressante a été mise au point par Kargin et ses collaborateurs.[20] Ces auteurs condensent sur une paroi froide, à la température de l'azote liquide, un mélange formé d'un monomère, d'un solvant et d' un métal volatile (Mg) ou d'un sel métallique. Le dépôt vitreux ainsi formé engendre une polymérisation très violente au cours du réchauffement.

III. CARACTÈRES CINÉTIQUES

A. Courbes de Conversion

La forme des courbes de conversion peut en principe apporter des renseignements précieux sur les différents processus qui se déroulent au cours d'une réaction. C'est ainsi qu'en cinétique classique, une courbe de conversion linéaire suggère l'existence d'un état quasi-stationnaire. Il n'en est plus de même dans les réactions en phase solide car des facteurs liés à la structure du milieu réactionnel peuvent devenir déterminants et conditionner toute la cinétique. Différentes formes de courbes de conversion ont été décrites pour les polymérisations en phase solide selon le monomère considéré: (*1*) des courbes de conversion sensiblement linéaires dans un grand domaine de conversions ont été signalées pour la polymérisation radiochimique du trioxane,[21] du styrène[22,23] et des mélanges solides de l'huile de paraffine avec le méthacrylate de méthyle[24*] ou le chlorure de vinyle;[26] de même, la polymérisation thermique des *p*-acétamido- et benzamidostyrène[17,18] est caractérisée par des courbes de conversion pratiquement linéaires; (*2*) des courbes de conversion autoaccélérées ont été observées pour la polymérisation radiochimique de l'acrylamide,[9,27] du diméthyl-2,4-styrène,[23] du *N*-vinylcarbazole,[28] et de la *N*-vinylsuccinimide[29] ainsi que pour la photopolymérisation de l'acide méthacrylique[15,16]; (*3*) enfin des courbes de conversion autoretardées ont été obtenues lors de la polymérisation radiochimique de l'acrylonitrile,[25,30,31] du formaldéhyde,[32,33] de l'acétaldéhyde,[32] de la β-propiolactone,[21,34] du dicétène,[21] et du bis-(chlorométhyl)-3,3-oxétane.[21,35]

La Figure 1 représente des exemples de ces trois types de courbes de conversion.

L'existence de courbes de conversion linéaires a parfois été interprétée comme l'indice d'un état quasi-stationnaire dans le système. Il nous paraît cependant difficile de partager ce point de vue. En effet, la faible mobilité des entités réactives dans le milieu cristallin doit gêner considérablement la réaction de terminaison et l'existence d'une post-polymérisation dans presque tous les systèmes montre directement que les chaînes croissantes ont une durée de vie très longue et que, par conséquent, l'état stationnaire ne peut s'établir qu'au bout d'un temps assez long. Il semble donc que les courbes de conversion linéaires observées dans certains cas ne soient que la conséquence d'une compensation de plusieurs facteurs cinétiques agissant en sens opposé.

En revanche, les courbes autoaccélérées cadrent bien avec l'idée exprimée ci-dessus d'une réaction progressant sans état stationnaire. Il faut remarquer que dans certains cas, les courbes de conversion présentent de véritables "périodes d'induction" suivies par la réaction accélérée proprement dite, la transition étant souvent très brusque [acrylamide,[27] vinyl-

* Les courbes de conversion accélérées mentionnées dans une publication antérieure[25] étaient la conséquence d'une inhibition par l'oxygène de l'air.

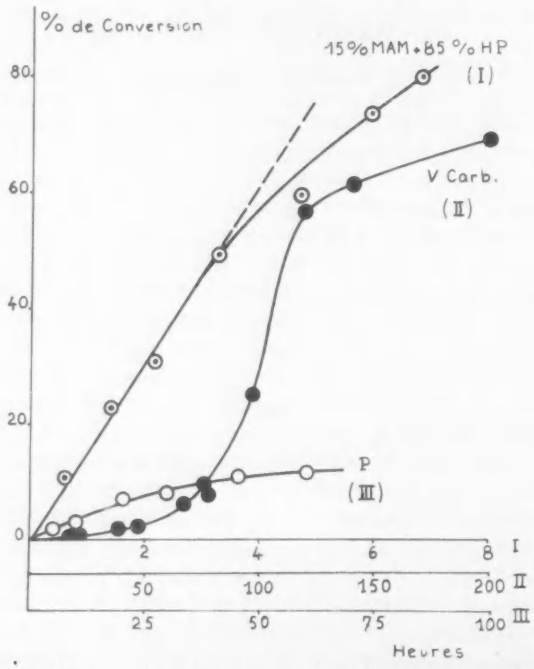

Fig. 1. Courbes de conversion obtenues pour les polymérisations radiochimiques à l'état solide: (*I*) mélange solide renfermant 15% de méthacrylate de méthyle et 85% d'huile de paraffine à −78°C; rayons gamma, 16,2 rads/sec.;[24] (*II*) vinylcarbazole à 20°C; rayons gamma; 61 rads/sec.;[28] (*III*) bis(chlorométhyl)-3,3-oxétane à 0°C; rayons gamma, 13,2 rads/sec.[35]

carbazole (Fig. 1)]. Si l'on remarque par ailleurs que pour certains de ces monomères la polymérisation procède plus rapidement dans des cristaux imparfaits ou déformés que dans des cristaux non déformés (voir le paragraphe V ci-dessous), il paraît raisonnable de supposer qu'une partie au moins de l'accélération observée résulte de la déformation du réseau par le polymère formé au cours de la réaction.

Au contraire, pour la plupart des monomères dont les courbes de conversion sont autoretardées, la polymérisation est d'autant plus rapide que les cristaux sont plus parfaits.[21,35] On peut donc penser que dans ce dernier cas, la déformation du réseau cristallin due à l'accumulation du polymère, gêne la réaction et celle-ci peut même s'arrêter totalement lorsqu'un taux de conversion critique a été atteint (courbe *III* de la Fig. 1) (voir aussi ci-dessous le paragraphe V).

B. Ordre par Rapport à la Vitesse d'Amorçage

Les modes d'amorçage photo- et radiochimiques permettent de comparer les vitesses de réaction obtenues avec des vitesses d'amorçage (intensités)

très différentes, sans que les autres conditions expérimentales telles que la qualité des cristaux ou la température de la réaction soient modifiées. De nombreux résultats ont ainsi été obtenus. Nous avons rassemblé dans le Tableau I les valeurs des exposants de l'intensité dans la relation:

$$V = KI^{\alpha}$$

trouvées pour une série de monomères polymérisés par voie radiochimique.

TABLEAU I

Valeurs Expérimentales des Exposants de l'Intensité et des Energies d'Activation Globales dans la Polymérisation Radiochimique de Quelques Monomères en Phase Solide

Monomère	α	$E\ddagger$, kcal/mole	Référence
Styrène	1,07	6,9–11,6	23, 25
Diméthyl-2,4-styrène	0,89	1–2	23
Acrylonitrile	1,0	0,3–1,0	25, 30, 31
Acrylamide	1,0[a]	3,0	9, 27
Acétate de vinyle (en phase vitreuse)	1,0	0	36
Stereate de vinyle	1,0	1,5	9, 37
Acide méthacrylique[b]	0,6	17,0	15
Methacrylate de méthyle (en solution solide dans l'huile de paraffine)	—	3,0	25
Méthacrylate de cétyle	1,0	—	29, 38
Butadiène	—	0,4	39
N-vinylcarbazole	0,6–0,75	7,0–12,0	28
N-vinylsuccinimide	0,6–0,7	12,7	29
Vinylpyrrolidone	1,25		40
Acenaphtylène	1,2	—	41
Cétène	1,0–1,2	−0,13	42
Dicétène	0,8[a]	0,11	21
β-propiolactone	0,9	6,3 et 0,8[c]	21
Formaldéhyde	0,65	−0,2 et 2,5[c]	32
Acétaldéhyde	1,0	5,0	32
Bis(chlorométhyl)-3,3-oxétane	1,0[a]	3,0 et 0,04[c]	21, 35, 43
Hexaméthylcyclotrisiloxane	1,0[a]	9,4	44, 45

[a] Décroit aux fortes intensités.

[b] Amorçage photochimique.

[c] Selon le domaine de températures considéré.

On voit que, pour de nombreux monomères, la polymérisation suit une loi de ler ordre par rapport à la vitesse d'amorçage. Quelques monomères présentent un exposant α compris entre 0,5 et 1. Enfin, dans certains cas, l'exposant α est supérieur à 1.

L'interprétation de ces résultats est très délicate. Plusieurs auteurs en ont conclu que selon que la valeur de α était plus voisine de 1 ou de 0,5 respectivement, la réaction de terminaison était principalement mono- ou bimoléculaire et ils en ont parfois tiré des arguments pour supporter tel ou tel mécanisme de réaction. Il faut noter cependant qu'une conclusion de ce genre suppose implicitement qu'un état quasi-stationnaire s'établit dans

le système et que les entités réactives (chaînes croissantes) diffusent librement dans le milieu ce qui n'est pas le cas pour les polymérisations en phase solide. Nous pensons que tant que le mécanisme intime de ces réactions n'est pas mieux connu, il faut se contenter de considérer ces valeurs comme des résultats empiriques, caractéristiques des différents systèmes étudies et vérifier si le schéma de réaction proposé n'est pas en contradiction avec ces valeurs.

L'existence d'exposants α supérieurs à 1 est particulièrement frappante. De tels exposants ne peuvent pas s'interpréter à l'aide d'un schéma cinétique classique. Une explication possible de ce phénomène peut être basée sur l'observation faite par certains auteurs,[29,32] selon laquelle les polymérisations en phase solide ne s'effectuent pas dans des conditions isothermes. En effet, la chaleur de la réaction ne peut se dissiper que très lentement dans le solide et des mesures directes de la température à l'intérieur du système ont montré que celle-ci dépassait souvent de plusieurs degrés la température extérieure. Il est évident que cette élévation de la température est d'autant plus grande que la réaction est plus rapide c'est à dire que la vitesse d'amorçage est elle-mème plus grande. Si le système examiné possède une énergie d'activation élevée, ce phénomène conduira à une vitesse d'autant plus élevée que la vitesse d'amorçage sera grande, et l'exposant α apparent pourra ainsi dépasser l'unité. Seules des expériences conduites en couches minces dans des conditions quasi-isothermes permettront de vérifier l'exactitude de l'hypothèse proposée ici.

C. Effet de la Température

La plupart des monomères qui se polymérisent en phase solide présentent une vitesse de réaction maximale juste en dessous de leur point de fusion (voir le paragraphe IV ci-dessous). Dans le solide, l'énergie d'activation globale est le plus souvent positive, bien que des valeurs légèrement négatives aient été observées dans quelques cas. Les énergies d'activation déterminées expérimentalement par les différents auteurs sont rassemblées dans le Tableau I. On voit que ces valeurs varient dans de larges limites selon le système considéré. Remarquons que ces énergies d'activation globales sont des grandeurs extrêmement complexes qui dépendent en particulier des mobilités des molécules de monomère dans le cristal, de la diffusion des chaînes croissantes, etc. Ont peut néanmoins distinguer grossièrement deux groupes de systèmes: ceux qui présentent une énergie d'activation très petite en valeur absolue (inférieure à 1–2 kcal/mole) et ceux dont l'énergie d'activation est nettement plus élevée. Il n'est pas exclu que ces deux groupes de monomères correspondent à des mecanismes de polymérisation différents.

D. Post-polymérisation

Si la polymérisation d'un monomère solide est amorcée par voie photo- ou radiochimique, il est possible d'étudier l'évolution de la réaction après la

fin de l'irradiation, lorsque la formation des centres initiateurs n'a plus lieu. (Nous admettons ici qu'il n'y a pas production d'un catalyseur sous l'influence de l'irradiation comme dans le cas de la photolyse de l'acétaldéhyde).

On a pu constater ainsi, dans presque tous les systèmes étudiés, que la polymérisation se poursuivait à l' "obscurité," souvent pendant des temps très longs, ce qui montre que certains des centres actifs (ou des chaînes croissantes) ont une durée de vie très longue. Des études ont été spécialement consacrées à ce phénomène.[46]

Nous ne discuterons pas ici toutes les conséquences de la post-polymérisation. Notons seulement une difficulté supplémentaire qu'elle introduit pour l'interprétation des expériences. Il faut noter, en effet, qu'à côté de la post-polymérisation que l'on peut étudier dans des conditions expérimentales bien définies, il est nécessaire de tenir compte du post-effet qui accompagne presque toujours la réaction principale. Ce dernier se manifeste en particulier au cours du traitement que l'on fait subir au mélange réactionnel pour séparer le polymère, c'est à dire au cours de la fusion ou de l'extraction du monomère par un solvant sélectif. Ces deux opérations ont pour conséquence de rendre plus mobiles les molécules de monomère qui étaient initialement figées dans le solide et il peut en résulter une polymérisation appréciable qui s'ajoute à la réaction qui a effectivement eu lieu pendant l'irradiation. L'importance de cette réaction "parasite" a pu être déterminée dans certains cas.[22,25,31,35]

Pour éviter cette difficulté, quelques auteurs ont cherché à mesurer directement la conversion, sans détruire l'édifice cristallin. L'étude de la cristallinité du monomère (par diffraction des rayons X) permet de résoudre ce problème dans une certaine mesure[21b,47] mais il est difficile de rendre cette méthode rigoureusement quantitative car le polymère formé présente parfois une orientation qui perturbe les mesures de diffraction. Plus récemment, la disparition du monomère non transformé a été dosée directement par l'étude des spectres d'absorption dans l'ultra-violet[16] et l'infrarouge.[17,18] Ces méthodes, très prometteuses pour tous les monomères vinyliques, devraient se généraliser dans l'avenir.

IV. INFLUENCE DU CHANGEMENT DE PHASE SOLIDE–LIQUIDE

Des renseignements extrêmement interessants peuvent être tirés d'une comparaison de la polymérisation en phase solide avec la réaction qui se produit dans le même système immédiatement au dessus de son point de fusion. Dans ce dernier cas, on peut appliquer les méthodes de la cinétique homogène classique, ce qui permet généralement de mieux comprendre le mécanisme de la réaction.

De nombreux systèmes ont été ainsi étudiés de part et d'autre de leur point de fusion. La plupart de ces études ont fait appel au mode d'amorçage radiochimique qui est d'un emploi particulièrement commode, mais qui entraîne, comme nous le verrons ci-dessous, des difficultés dans l'interprétation des données expérimentales.

D'après les résultats obtenus, on peut classer les différents monomères en quatre groupes selon leur comportement cinétique de part et d'autre du point de fusion.*

A. Premier Groupe

Les monomères du ler groupe se polymérisent beaucoup plus rapidement en phase solide qu'immédiatement au-dessus de leur point de fusion. Parmi les représentants les plus caractéristiques de ce groupe citons: le styrène,[22,23] le diméthyl-2,4-styrène,[23] l'acrylonitrile,[25,31,49] le méthacrylonitrile,[50] et le formaldéhyde.[32,33,51] Les courbes (St) et (AN) de la Figure 2 représentent à titre d'exemples les diagrammes d'Arrhénius obtenus avec le styrène et l'acrylonitrile.

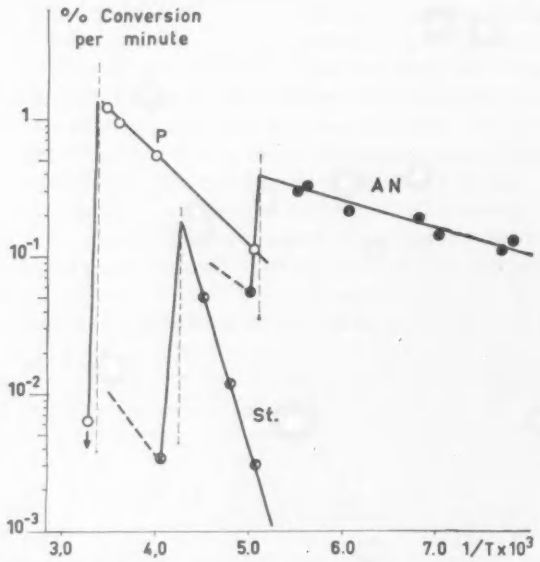

Fig. 2. Diagrammes d'Arrhénius de la polymérisation de différents monomères au voisinage de leur point de fusion: (*st*) styrène;[25] (*AN*) acrylonitrile,[25] (*P*) bis(chlorométhyl)-3,3-oxétane.[35]

L'accélération brutale de la réaction au passage du liquide au solide peut en principe s'expliquer de deux façons différentes: (*1*) on peut admettre que le même mécanisme réactionnel a lieu dans les deux phases mais que, dans la phase solide, la réaction est favorisée par l'absence de la terminaison des chaînes ou encore par une propagation plus rapide, due par exemple à une orientation particulièrement favorable des molécules de monomère

* Dans une publication antérieure,[48] nous avions distingué un cinquième groupe de monomères mais cette distinction était essentiellement basée sur un comportement particulier dû à l'amorçage radiochimique.

dans le réseau; (*2*) on peut penser qu'à la polymérisation radicalaire qui a lieu en phase liquide s'ajoute, en phase solide, un processus ionique. On admet, en effet, que les ions formés par radiolyse dans un liquide n'ont qu'une durée de vie très brève car la plupart des électrons sont rapidement recaptés par leur ion parent; au contraire, en phase solide, les électrons peuvent être "piégés" dans des défauts du réseau ce qui prolonge considérablement la durée de vie des ions et favorise ainsi l'amorçage d'un processus ionique.

Pour trancher entre ces deux explications, il faudrait par exemple étudier le comportement de ces systèmes avec un autre mode d'amorçage qui ne créerait que des radicaux libres (amorçage photo-sensibilisé). Aucune expérience de ce genre n'a encore été effectuée à notre connaissance.

B. Deuxième Groupe

Les monomères du 2ème groupe se polymérisent seulement lorsqu'ils sont irradiés en phase solide; en phase liquide l'irradiation ne conduit qu'à des oligomères de bas poids moléculaire. Ce groupe comprend: l'hexaméthylcyclotrisiloxane,[44,45*] la β-propiolactone,[21] le dicétène,[21] le trioxane,[21] et le bis(chlorométhyl)-3,3-oxétane[21,35] (courbe *P* de la Fig. 2).

Etant donné que tous ces monomères ne sont polymérisables qu'à l'aide de catalyseurs ioniques, il parait justifié d'appliquer à ces systèmes l'interpretation proposée dans le paragraphe A-(2) ci-dessus, à savoir que cette polymérisation est ionique et que l'amorçage ionique par les radiations ionisantes est favorisé à l'état solide par la stabilisation des ions de signes contraires. La seule constatation de l'accélération observée au passage du liquide à la phase cristalline ne nous apporte donc pas de renseignements sur le rôle éventuel joué par une orientation favorable des molécules de monomère dans le réseau, puisque cette accélération ne serait que la conséquence du mode d'amorçage radiochimique utilisé. Comme par ailleurs la polymérisation de certains de ces monomères [bis(chlorométhyl)-3,3-oxétane, trioxane] a également été initiée avec succès en phase solide par des catalyseurs ioniques,[13,14] il serait intéressant d'effectuer une étude parallèle avec ces catalyseurs dans les deux phases liquide et solide.

C. Troisième Groupe

Les monomères du 3ème groupe se polymérisent beaucoup plus lentement en phase solide que dans le liquide. Pour certains représentants de ce groupe, on n'observe aucune polymérisation en phase cristalline mais seulement une post-polymérisation au moment du réchauffement, la réaction étant amorcée par les radicaux gelés présents dans le solide irradié. Ce groupe comprend: le méthacrylate de méthyle, l'acrylate de méthyle, l'acétate de vinyle et le chlorure de vinyle. La courbe φ de la Figure 3 représente le diagramme d'Arrhénius obtenu avec l'acétate de vinyle. On

* Selon des expériences récentes,[52] ce monomère se polymériserait ègalement par irradiation en phase liquide.

peut remarquer que le comportement de ces monomères est celui que l'on aurait pu prévoir pour un processus radicalaire dans lequel on aurait figé brusquement les molécules interessées par la réaction. On peut en effet penser à priori que la propagation des chaînes est peu probable en phase solide. Il a pourtant été trouvé que tous les monomères cités ci-dessus se polymérisent si l'on irradie une dispersion du monomère dans un liquide visqueux, capable de former un verre à basse température (huile de paraffine),[24–26] ou encore si l'on peut obtenir un verre en refroidissant brusquement le monomère liquide.[36] La Figure 3 montre l'influence d'une telle trempe dans le cas de l'acétate de vinyle (ce système est par ailleurs décrit

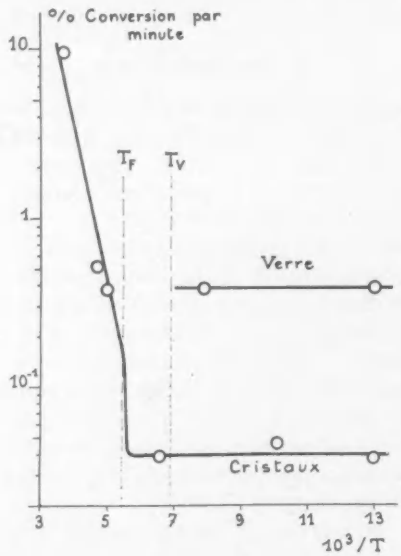

Fig. 3. Diagramme d'Arrhénius de la polymérisation de l'acétate de vinyle amorcée par des électrons accélérés; courbe supérieure: phase vitreuse; courbe inférieure: phase cristalline (d'après Barkalov et al.[36]).

par les mêmes auteurs dans une communication à ce Symposium).[53] La Figure 4 représente l'influence de l'addition d'huile de paraffine sur la vitesse de polymérisation radiochimique des quatre monomères précédemment cités à $-78°$. Mentionnons encore que si l'on choisit un ester de l'acide méthacrylique dans lequel le reste alcoolique possède une longue chaîne hydrocarbonée, la polymérisation s'effectue dans le monomère pur congelé en absence de tout additif; tel est le cas du méthacrylate de céthyle[29,38] (voir aussi la communication de Hardy et al. à ce Symposium[54]).

Il semble que dans tous les cas précédents, la réaction procède par un mécanisme radicalaire et que la viscosité élevée du verre favorise la réaction, en empêchant la terminaison des chaînes.

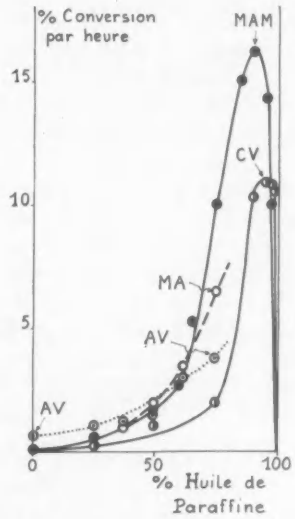

Fig. 4. Influence de la concentration de l'huile de paraffine sur la vitesse de polymérisation des monomères suivants en solution solide: (*MAM*) méthacrylate de méthyle;[24] (*AM*) acrylate de méthyle (conversion par 5 h);[24] (*AV*) acétate de vinyle;[24] (*CV*) chlorure de vinyle.[26] Irradiation à −78°; rayons gamma, 16,2 rads/sec.

D. Quatrième Groupe

Les monomères du 4ème groupe se polymérisent avec des vitesses peu différentes dans les deux phases. Le passage du liquide au solide ne produit qu'une légère discontinuité sur le diagramme d'Arrhénius, cette dernière pouvant être positive ou négative. Parmi les représentants de ce groupe, on peut citer: le stéarate de vinyle,[9,37] le vinylcarbazole,[28] et la vinylpyrrolidone.[40] La Figure 5 représente les diagrammes d'Arrhénius obtenus pour la vinylpyrrolidone avec trois intensités différentes des rayons gamma. On peut voir que la chute de la vitesse au passage du liquide au solide est d'autant moins marquée que l'intensité du rayonnement est plus forte. Ceci résulte du fait que l'exposant α de l'intensité est égal à 0,5 en phase liquide et à 1,25 dans le solide (voir Tableau I). Pour les intensités très élevées, on peut même prévoir que la vitesse sera plus grande dans le solide que dans le liquide. Cette constatation montre que la classification proposée ci-dessus est dans une certaine mesure arbitraire, tout au moins en ce qui concerne les monomères des groupes 4 et 1, pour lesquels la distinction peut en fait dépendre des conditions expérimentales utilisées.

De ce qui précède, on peut conclure que l'immobilisation des molécules de monomères dans des positions géométriques bien déterminées d'un réseau cristallin peut être favorable pour la réaction (en particulier si la disposition du monomère et son orientation préfigurent le polymère), défavorable (cas des monomères du troisième groupe) ou indifférente (quatri-

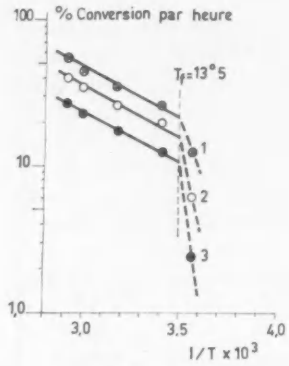

Fig. 5. Diagrammes d'Arrhénius de la polymérisation de la vinylpyrrolidone soumise aux rayons gamma:[40] (*1*) 61,0 rads/sec; (*2*) 37,4 rads/sec; (*3*) 17,7 rads/sec.

ème groupe). Cependant la constatation d'une accélération en phase solide pour la polymérisation radiochimique des monomères du premier et deuxième groupes ne permet pas de conclure sur un rôle de l'orientation car cette accélération peut résulter de la contribution d'un processus ionique qui se produirait préférentiellement en phase solide.

V. FACTEURS LIÉS Á LA STRUCTURE CRISTALLINE DU MONOMÈRE

Divers auteurs ont signalé que la polymérisation en phase cristalline était influencée par la qualité des cristaux de monomère utilisés. Plusieurs techniques ont été employées pour mettre ce phénomène en évidence, la qualité des cristaux pouvant être modifiée par la vitesse de cristallisation, par un traitement mécanique ou physico-chimique, par l'introduction d'une substance étrangère, etc.

A. "Grands" et "Petits" Cristaux

Les monomères suivants: trioxane,[21] bis(chlorométhyl)-3,3-oxétane,[21,35] acétaldéhyde,[32] et acrylonitrile,[31] se polymérisent mieux lorsqu'on soumet à l'irradiation (rayons X ou gamma) de gros cristaux de monomère, obtenus par cristallisation lente, que des petits cristaux obtenus par trempe rapide. Dans les grande cristaux, la réaction est plus rapide, la conversion finale peut être plus grande,[21,35] et parfois le polymère obtenu possède une densité et un point de fusion plus élevés.[55] Au contraire, l'amide acrylique se polymérise plus vite lorsqu'on conduit la réaction dans un agglomérat de petits cristaux que dans des monocristaux de grandes dimensions.[46,56]

B. Cristaux Déformés

Avec l'acrylamide, on a également observé que des monocristaux déformés, on rayés par un outil, donnaient lieu à une polymérisation plus

rapide que les cristaux qui n'avaient pas subi un tel traitement.[56] Il semble donc que, pour ce monomère, la présence d'un réseau trop parfait gêne la polymérisation. On peut également rapprocher de ce résultat le fait que les courbes de conversion sont autoaccélérées (voir ci-dessus), ce qui suggère que la perturbation causée dans le cristal par l'accumulation du polymère produit elle aussi un effet d'accélération (voir aussi Adler et al.[56]).

Au contraire, pour d'autres monomères, la polymérisation est ralentie en presence d'additifs étrangers qui vraisemblablement déforment le réseau cristallin. Tel est le cas de l'acrylonitrile[25] et du bis(chlorométhyl)-3,3-oxétane.[35] Ces monomères donnent par ailleurs des courbes de conversion autoretardées (voir Fig. 1).

Une observation intéressante a été faite au cours de la photopolymérisation des acides acrylique et méthacrylique. Si l'on exerce une pression sur un monocristal de l'un ou l'autre de ces deux monomères, la polymérisation est fortement retardée.[16] Ce résultat a été interprété en admettant que la polymérisation se produisait principalement le long des dislocations présentes dans le cristal et qu'une certaine mobilité de ces dislocations était requise pour la reaction. L'effet de la pression serait de grouper toutes les dislocations ou encore de les immobiliser, ce qui aurait pour conséquence de gêner la propagation des chaînes.

C. Influence de la Nature de la Maille Cristalline

Trop peu de données existent actuellement sur la structure des mailles cristallines des différents monomères. Des études dans ce sens sont pourtant nécessaires si nous voulons espérer comprendre le mécanisme intime des polymérisations en phase solide. Dans le cas de l'acétaldéhyde[5] et des monomères hétérocycliques,[21b] il a été montré que l'orientation du monomère dans le cristal préfigurait pratiquement la structure du polymère. Pour d'autres monomères, il existe seulement des données indirectes qui montrent l'importance de la structure cristalline. C'est ainsi que des vitesses de polymérisation très différentes ont été observées pour différents sels de l'acide acrylique, bien que les porteurs de chaînes aient dans tous les cas la même structure chimique.[57] De plus, l'acrylate de calcium forme deux cristaux hydratés: un monohydrate et un dihydrate et le dihydrate se polymérise beaucoup plus facilement que le monohydrate.[17,58] Ici encore, on ne peut comprendre ce résultat qu'en admettant que la structure cristalline du dihydrate est particulièrement favorable à la polymérisation.

D. Transitions Solide–Solide

L'acrylonitrile solide possède un point de transition de ler ordre à $-113°C$.[59,60] De part et d'autre de celui-ci existent deux formes cristallines différentes: une forme "basse température" et une forme "haute température." Si l'on cristallise sans précautions spéciales le monomère à $-196°$, on obtient un mélange des deux formes cristallines et seul un recuit prolongé à $-120°C$ permet d'isoler la forme "basse température" à l'état "pur." Il a été montre ainsi que la polymérisation est beaucoup plus lente

dans la phase "basse température."[61] Cette constatation permet d'expliquer la cassure observée antérieruement dans le diagramme d'Arrhénius pour la polymérisation de ce monomère en phase solide.[25] Un phénomène analogue se produit probablement dans le cas de la β-propiolactone,[21] du formaldéhyde,[32,51] du méthacrylate de céthyle[29,38] et du bis(chlorométhyl)-3,3-oxétane[43] pour lesquels on a également signalé des cassures dans les diagrammes d'Arrhénius. Les transitions solide–solide jouent également un rôle très important dans d'autres processus chimique, en phase solide.[59]

E. Polymérisations et Copolymérisations dans des Solutions Solides

L'acrylamide et le propionamide sont isomorphes et ces deux substances syncristallisent en toutes proportions. Cette circonstance a été mise à profit par deux groupes de chercheurs[27,46] qui ont étudié la polymérisation dans des cristaux mixtes. La réaction était amorcée par les rayons gamma. Il a été ainsi trouvé que l'addition de propionamide au monomère conduisait à un accroissement de la vitesse de polymérisation et à une diminution de la masse moléculaire du polymère forme. L'addition d'acétamide, non isomorphe de l'acrylamide, produisait une accélération encore plus importante mais n'affectait que légèrement la masse moléculaire.

L'effet accélérateur de ces additifs peut s'expliquer par une perturbation du réseau de l'acrylamide puisque, comme nous l'avons vu ci-dessus, la réaction est plus rapide dans des cristaux imparfaits de ce monomère. L'effet des additifs sur les masses moléculaires est beaucoup plus difficile à comprendre car le mécanisme de la terminaison des chaînes croissantes n'est pas connu. Une réaction de transfert de chaîne a été invoquée pour expliquer les résultats expérimentaux.[46]

Un autre exemple d'accélération par un additif en phase solide nous est fourni par les mélanges des monomères du troisième groupe avec l'huile de paraffine (voir le paragraphe IV ci-dessus). La Figure 4 montre cet effet dans le cas du méthacrylate de méthyle, de l'acrylate de méthyle, de l'acétate de vinyle et du chlorure de vinyle. Tous ces mélanges étaient irradiés à −78°C; à cette temperature, seul le methacrylate de méthyle est solide, les trois derniers monomères sont liquides. Cependant tous les mélanges formaient des verres parfaitement transparents pour des teneurs suffisamment élevées en huile de paraffine (superieures à 90%). On voit que c'est précisément dans ce domaine de concentrations que les vitesses sont maximales. Les masses moleculaires du poly(méthacrylate de méthyle) obtenu suivent une courbe de même forme.[25] Il est donc permis de penser que la structure vitreuse du milieu favorise la propagation des chaînes, réaction qui ne se produit pratiquement pas dans le monomère pur cristallisé. Il est intéressant de noter que même pour des concentrations extrêmement petites du monomère dans le verre (1% pour le chlorure de vinyle), la polymérisation a encore lieu avec une vitesse appréciable.

Quelques indications existent également sur la polymérisation de la β-propiolactone dans des mélanges solides avec le méthanol[21] et sur celle du vinylcarbazole dans des mélanges avec le benzène.[28] Différents composés

ont été ajoutes au styrène,[22,25] à l'acrylonitrile,[25] au trioxane,[21] et au bis-(chlorométhyl)-3,3-oxétane.[35]

Enfin des copolymérisations ont été tentées en phase solide. Dans ces études les auteurs ont en général congelé les mélanges des deux monomères sans connaître les conditions exactes de la cristallisation. Les monomères suivants ont été ainsi copolymérisés avec la β-propiolactone: acrylonitrile, dicétène et γ-butyrolactone.[21] Le dicétène et le diméthylcétène ont été copolymérisés avec l'acrylonitrile[21] ainsi qu'avec différents aldéhydes, des cétones, des esters formiques, et quelques autres composés.[62] Un mélange de deux monomères isomorphes et formant des cristaux mixtes: l'acrylamide et le methacrylamide a également été copolymérisé.[63]

Les vitesses de copolymérisation observées par les différents auteurs présentent en général des minimums ou des maximums pour une certaine composition du mélange initial. Des courbes de composition des copolymères obtenus ont été publiées.[21] Toutes ces études sont encore à un stade préliminaire mais elles ouvrent un champ d'investigation extrêmement vaste et peu exploré.

VI. NATURE DES ENTITÉS RÉACTIVES RESPONSABLES DE LA PROPAGATION DES CHAÎNES

Dans certaines expériences de polymérisation en phase solide, la nature des porteurs de chaînes est bien déterminée. C'est ainsi que le processus est sans aucun doute radicalaire dans la polymérisation thermique de l'acrylamide renfermant de l'azobisisobutyronitrile,[11] la polymérisation de l'acide méthacrylique photosensibilisée par ce même composé,[15] et la polymérisation thermique des *p*-acétamido- et *p*-benzamidostyrène.[17,18] Par ailleurs, un processus ionique est certainement responsable de la polymérisation du bis(chlorométhyl)-3,3-oxétane,[13] du trioxane,[14] et de l'α-methylstyrène[12] soumis à l'action de BF_3 ou à d'autres acides de Lewis. Par contre, dans les expériences radiochimiques, la nature des porteurs de chaîne est moins certaine. Ce point a déjà été brièvement mentionné dans le paragraphe IV. Remarquons qu'une des difficultés à laquelle on se heurte lorsqu'on essaye de comprendre le mécanisme d'une réaction en phase solide est que les méthodes classiques utilisées pour la cinétique des réactions homogènes ne sont généralement pas applicables. Nous avons déjà vu ci-dessus qu'on ne peut tirer aucune conclusion définitive de l'ordre de la réaction par rapport à la vitesse d'amorçage. Il en est de même si l'on veut utiliser des inhibiteurs sélectifs capables d'intercepter les radicaux libres ou les ions. En effet, si ces inhibiteurs sont congelés en même temps que le monomère, ils ne seront généralement pas distribués d'une manière uniforme dans le milieu; comme d'autre part, de tels additifs ne peuvent pas diffuser rapidement dans le solide, on ne pourra pas être certain qu'ils soient en mesure d'agir efficacement sur le lieu même de la réaction. Enfin, l'addition d'un inhibiteur peut modifier les conditions de cristallisation du monomère et ainsi avoir une action parfois imprévue

sur la réaction. Il faut noter toutefois que si l'on a la chance d'observer une action positive avec un, ou mieux plusieurs inhibiteurs d'un même type, il sera possible d'en tirer une conclusion sur le mécanisme de la réaction, à condition que la concentration de l'inhibiteur soit suffisamment petite pour ne pas perturber la qualité du réseau cristallin. Un cas particulier est représenté par les systèmes vitreux ou cette dernière difficulté n'est pas à craindre. C'est ainsi que l'inhibition de la polymérisation des solutions solides de méthacrylate de méthyle dans l'huile de paraffine par la benzoquinone et l'oxygène[24,25] fournit un argument valable pour supporter l'existence d'un mècanisme radicalaire dans ce système.

La composition d'un copolymère obtenu à partir d'un système homogène pourrait également fournir des données intéressantes. Mais cette technique n'a été que très peu exploitée jusqu'à prèsent.

La distinction entre polymérisations radicalaire ou ionique est assez simple pour les monomères qui ne peuvent se polymériser que par l'un ou l'autre de ces deux mécanismes. C'est ainsi que la reaction est certainement ionique dans le cas des composés hétero-cycliques (renfermant de l'oxygène) pour lesquels une réaction de propagation en chaîne radicalaire est difficile à imaginer. Il est intéressant de noter que tous ces composés font partie du 2ème groupe défini dans le paragraphe IV-B ci-dessus.

Dans tous les cas examinés, il est difficile de comprendre dans le détail les processus qui conduisent à un polymère en phase solide. Aussi a-t-on parfois invoqué des mécanismes de propagation inconnus en phase liquide, mettant par exemple en jeu des entités excitées. L'idée d'effets collectifs se produisant dans le cristal avec une accumulation de l'énergie dégagée par la réaction à chaque étape de la propagation[64] rentre dans cette catégorie d'hypothèses. Aucune donnée expérimentale directe ne nous permet pour le moment de confirmer ou d'infirmer un tel point de vue.

VII. MÉCHANISME DE LA CROISSANCE DES CHAÎNES EN PHASE SOLIDE

Le fait qu'une réaction en chaîne puisse se produire dans une phase cristalline est surprenant en lui-même. En effet, dans la plupart des cas, les distances entre les molécules de monomère dépassent largement la longueur des liaisons qui doivent se former et un déplacement du monomère sur plusieurs angströms est souvent nécessaire pour que la propagation puisse se produire. Dans d'autres cas, au contraire, la disposition du monomère dans le réseau peut être particulièrement favorable à tel point qu'une très légère translation ou une simple torsion de la molécule suffit pour donner naissance au polymère.

L'examen de la structure des polymères formés à partir des monomères solides permet également de distinguer deux cas extrêmes. Dans certains systèmes, les polymères sont parfaitement orientés, généralement le long d'un axe privilégié du cristal de monomère et peuvent même prendre naissance sous forme de fibres.[2,21b] Dans d'autres cas, au contraire, le

polymère formé est entièrement désordonné et ne se distingue en rien du polymère formé en phase liquide. Ces constatations suggèrent l'existence de deux mécanismes de polymérisation diamétralement opposés.

A. Propagation Contrôlée par le Réseau

Dans un premier groupe de systèmes, le polymère est formé comme dans un moule, à l'intérieur du réseau du monomère. L'étude cristallographique de certains des systèmes correspondants montre que l'arrangement des molécules de monomère préfigure la structure du polymère, seul un très léger déplacement étant requis pour engendrer le passage de l'un à l'autre. Tel est le cas en particulier du trioxane et d'autres monomères hétérocycliques où les molécules sont empilées régulièrement les unes au dessus des autres, en formant des colonnes. L'ouverture d'un cycle, suivie d'une légère torsion, met la molécule en position favorable pour reagir avec ses voisines, ce qui transforme progressivement l'empilement des cycles en une structure hélicoïdale polymérique.[21b] Une situation analogue se retrouve dans l'acétaldehyde, où une très légère translation est suffisante pour assurer la propagation.[5] De même les *p*-acétamido- et *p*-benzamidostyrène possèdent une structure dans laquelle les groupes vinyliques sont disposés dans des feuillets minces séparés les uns des autres par des distances plus grandes qui correspondent à l'empilement des volumineux substituants amidostyryles.[17,18] La polymérisation serait localisée dans ces couches parallèles et l'orientation serait ici encore imposée par le réseau cristallin.

B. Propagation Désordonnée

L'autre cas extrême nous est fourni par les systèmes dans lesquels la polymérisation a lieu dans un milieu parfaitement organisé mais où le polymère formé ne semble porter aucune marque de cette organisation. Un tel comportement s'observe en particulier pour certains monomères vinyliques comme le styrène et l'acrylamide. Il est important de noter que la polymérisation de ces monomères s'accompagne d'une contraction notable du milieu réactionnel en raison de la différence entre les densités du monomère et du polymère, et cette remarque permet peut-être de comprendre la raison de la propagation désordonnée dans ces systèmes. En effet, par suite de la contraction qui doit se manifester à chaque étape de la propagation, l'extrêmité active de la chaîne croissante se trouve rapidement dans une cavité. A partir de ce moment, la propagation ne peut plus se faire qu'au dépens des molécules du monomère qui tapissent les parois de cette cavité et qui doivent par conséquent se sublimer et parcourir un certain trajet dans le vide avant de pouvoir réagir avec la chaîne croissante. Ce type de polymérisation se rapproche donc, dans une certaine mesure des polymérisations en phase gazeuse et il n'est pas étonnant que l'on obtienne un polymère qui ne présente pas de structure organisée. L'énergie mise en jeu pour extraire le monomère des parois de la cavité est certainement inférieure à l'énergie de sublimation du monomère corres-

pondant car le réseau doit être fortement déformé au voisinage de la molécule de polymère en raison des tensions provoquées lors de la formation de ce dernier.

Remarquons enfin que l'hypothèse précédente peut rendre compte de l'autoaccélération observée pour les monomères qui se polymérisent mieux dans des cristaux imparfaits (acrylamide; voir le paragraphe V). En effet, si la polymérisation a principalement lieu dans de telles cavités, elle doit être favorisée par des défauts cristallins (lacunes, dislocations) qui peuvent faciliter la croissances des chaînes au début de la reaction.

C. Gas Général

Il est permis de penser que la plupart des systèmes se placent en réalité entre les deux cas extrêmes examinés ci-dessus. En effet, l'influence du réseau sur la réaction de propagation doit dépendre des parametres cristallins, de l'orientation de la molécule de monomère dans la maille et de sa mobilité, de la réactivité du monomère, etc., et il est peu probable que tous ces différents facteurs exercent une action conjuguée dans tous les cas. De même, si la propagation a lieu dans une cavité, le réseau pourra néanmoins avoir une certaine influence sur la reaction en favorisant par exemple une addition plus régulière "tête à queue." On peut noter à ce sujet qu'un certain degré d'ordre a été mis en évidence par une méthode indirecte dans le polyacrylonitrile obtenu par irradiation du monomère à $-196°C$.[65]

Enfin, il ne faut pas perdre de vue le fait que les différents systèmes dont on a étudié la polymérisation en phase solide comprennent en réalité toute une série de variantes qui se distinguent nettement des deux cas extrêmes examinés ci-dessus. C'est le cas, en particulier des milieux vitreux. Ces derniers représentent un cas intermédiaire entre les édifices cristallins et les liquides. Peu d'études existent dans ce domaine et nos connaissances sur la structure des verres sont encore plus rudimentaires que sur les cristaux. Cependant, il apparaît que les structures vitreuses peuvent rendre la polymérisation plus facile. De plus, elles permettront peut-être d'étudier des mélanges de monomères en phase solide dans des conditions particulièrement favorables du point de vue de leur homogénéité. Il est évident que de nombreuses expériences sont nécessaires pour eclaircir les différents problèmes soulevés par tous ces systèmes.

VIII. CONCLUSION

D'après ce qui précède, on peut voir que l'étude des polymérisations en phase solide entre maintenant dans une étape critique. Des résultats intéressants ont été acquis mais leur interprétation est souvent difficile. Des techniques nouvelles devront être mises en oeuvre pour accroître nos connaissances sur la nature des réactions qui se produisent et sur les mécanismes mis en jeu. Ces techniques font autant appel à la physique du solide qu'à la chimie proprement dite. Aussi, une collaboration étroite entre chimistes et physiciens est-elle particulièrement souhaitable dans ce

domaine afin d'aboutir à une meilleure compréhension des différents processus complexes mis en jeu.

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Discussion

H. Morawetz (*Polytechnic Institute of Brooklyn, N. Y., U.S.A.*): It is unfortunate that so few kinetic data on solid state polymerization are supplemented by molecular weight data. Dr. Chapiro has cited results (ref. 46) showing that the post-polymerization of irradiated acrylamide is faster in small crystals. However by following both the reaction rate and the time dependence of the molecular weight it could be shown that crystal size affects in this case only the number of growing chains, not the rate of growth of the individual chain.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1571–1587

Some Novel Initiators of Vinyl Polymerization

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1. INTRODUCTION

The investigation of new systems for the initiation of polymerization is not merely of academic interest, but is of potential practical value insofar as the discovery of new initiators may lead to the possibility of preparing polymers with novel properties. Ziegler-Natta catalysis is, of course, the outstanding example of a technique of polymerization which produces polymers with properties previously unobtainable. However, it should be realized that initiators of the more conventional types of polymerization may be of practical value if they are able to function under unusual conditions, e.g., at temperatures low enough to permit the development of stereoregularity or to ensure the virtual absence of chain branching. We believe, therefore, that efforts to develop new initiators constitute a worthwhile activity in the field of polymer science, and in this report we describe investigations of this type. The systems studied are mainly based on metal carbonyls, but some other organometallic compounds are also included.

2. METAL CARBONYLS AS INITIATORS OF POLYMERIZATION

2.1. General

Our interest in these compounds was stimulated by the observations of Freydlina and Belyavskiĭ[1] which showed that the telomerization of ethylene with carbon tetrachloride at 100°C. could be catalyzed by the hexacarbonyls of the Group VI elements Cr, Mo, W, or by $Fe(CO)_5$. Although these workers made no reference to the possible use of the carbonyls as polymerization initiators, it seemed clear that, if the telomerization process proceeded by the conventional reactions, suitable adjustment of the experimental conditions should lead to the formation of high polymers, rather than telomers. Preliminary experiments with $Cr(CO)_6$, $Mo(Co)_6$, $W(CO)_6$ and several monomers such as methyl methacrylate, styrene, and acrylonitrile at temperatures up to 100°C. failed to reveal any significant initiating potentialities. However, any one of these carbonyls together with a low concentration of a suitable organic halogen derivative, e.g., CCl_4, functioned as an active initiator.[2,3] Some results for the carbonyls

TABLE I

Activities of Various Halides in Initiating Polymerization of Methyl Methacrylate at 100°C. in the Presence of a Group VI Metal Carbonyl[a]

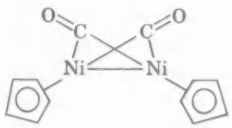
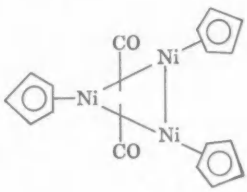
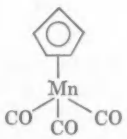
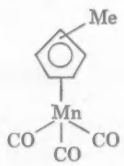
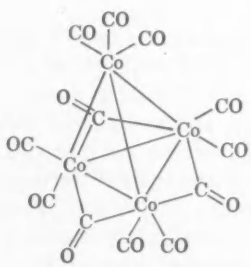
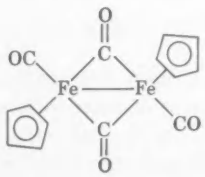
Halogen compound	Conversion, %		
	$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$
None	2.8	1.1	2.0
Cl_3C—			
—H	6.2	6.8	3.1
—F	3.5	9.2	4.1
—Cl	11.2	29.3	10.4
—Br	13.1	51.2	13.5
—CHO	13.2	33.8	6.5
$—CH_2Cl$	6.7	11.9	8.6
$—NO_2$	0.8	12.3	1.7
—COOH	18.1	92.5	8.5
$—CH_3$	4.4	9.0	4.4
$—CHCl_2$	7.4	17.5	27.6
—CN	21.3	100	11.1
$—CH_2OH$	6.4	11.5	—
—CH(OH)OEt	18.0	44.8	8.6
$—C_6H_5$	27.6	70.5	11.6
$—C_6H_4F(3)$	3.9	76.2	8.9
$—C_6H_4Cl(2)$	20.3	88.7	11.1
$—C_6H_4Cl(4)$	19.8	68.3	14.2
$—C_6H_3Cl_2(2,4)$[b]	22.0	93.2	2.1
$C_6H_3Cl_2(3,4)$	25.1	90.0	13.4
Cl_2CH—			
—H	1.8	—	—
—COOH	10.0	11.9	4.5
$—CHCl_2$	3.0	6.0	4.0
—CN	11.2	67.0	7.8
CCl_2F_2	—	1.0	—
Br_3C—			
—H	14.8	32.8	—
—Br[b]	13.1	52.6	8.3
—CHO	0	1.9	0
CHI_3[b]	Trace	Trace	—
CF_3COOH	Trace	—	—
CH_2Br_2	0.7	—	—

[a] A 9.5 ml. portion of monomer was heated for 30 min. with 30 mg. carbonyl and 0.5 ml. liquid or 0.8 g. solid halogen compound.

[b] Solid compound.

of the Group VI elements are shown in Table I. It has been pointed out that, in general, halides containing three or four chlorine or bromine atoms joined to a single carbon atom are the most active.[2,3] However, the activity of a halide would be expected to be inversely related to the stability of the radical formed by scission of a halogen atom, so that the order of activity would be $CCl_4 > CHCl_3 > CH_2Cl_2$. The high activities of CCl_3COOH and CCl_3CN may perhaps be explained in this way, and also that of $CHCl_2COOH$ compared to CH_2Cl_2. Fluorine and iodine derivatives are

TABLE II

Formula	Structure
$[(C_5H_5)NiCO]_2$	
$(C_5H_5)_2Ni_3(CO)_2$	
$(C_5H_5)Mn(CO)_3$	
$(C_5H_4CH_3)Mn(CO)_3$	
$Co_4(CO)_{12}$	
$(C_5H_5)_2Fe_2(CO)_4$	

not effective; the latter liberate iodine, which is a powerful retarder. Negative results have been obtained with $RSiCl_3$ compounds, probably on account of the relatively high Si—Cl bond energy.

Molybdenum hexacarbonyl is a much more active initiator than the corresponding Cr and W compounds.

A number of other carbonyls have also been studied:[4–7] the simple carbonyls $Mn_2(CO)_{10}$, $Ni(CO)_4$, $Co_2(CO)_8$ and the more complex derivatives with the formulae and structures shown in Table II.

All these carbonyls, with the sole exception of $Co_2(CO)_8$, which will be mentioned later, can initiate polymerization effectively in the presence of suitable halides. It is interesting to note that $[(C_5H_5)NiCO]_2$ and $(C_5H_5)_3Ni_3(CO)_2$ contain only CO groups which bridge two or more metal atoms. The activity of these compounds, therefore, suggests that the ability to initiate is not connected with any specific structural features in the molecule; the mere presence of a carbonyl group seems to suffice.

Most of the work to be described has been carried out with methyl methacrylate as the monomer. A few experiments with styrene and acrylonitrile have shown that the rate of initiation by a given carbonyl–halide combination depends on the nature of the monomer; thus, for example, $Cr(CO)_6$–CCl_4 and $W(CO)_6$–CCl_4 are unable to initiate the polymerization of styrene to a significant extent. Further investigation of this matter is desirable.

2.2. Kinetic Observations

The carbonyls for which kinetic data are available show a similar pattern of behavior, with some quantitative differences. We shall now describe the main features.

2.21. Type of Polymerization. Figure 1 indicates that at 100 and 80°C. the rate of polymerization of methyl methacrylate initiated by $Cr(CO)_6$–CCl_4 is proportional to $[Cr(CO)_6]^{1/2}$ at constant $[CCl_4]$. This is a general feature of these reactions and is consistent with the idea that the polymerization proceeds through free radical intermediates. A similar conclusion may be drawn from measurements of the degrees of polymerization. If ν is the kinetic chain length, which may be calculated from the number-average degree of polymerization by making a (small) correction for chain transfer to halide and monomer, we have, for a free-radical reaction,

$$-\nu\,(d[M]/dt) = k_p^2[M]^2/k_t \qquad (1)$$

where [M] is the monomer concentration, and k_p, k_t the velocity coefficients of propagation and termination (disproportionation), respectively. This relation allows $k_p/k_t^{1/2}$ to be estimated. It turns out that the values obtained with the carbonyls are consistent between themselves and agree satisfactorily with the literature values for methyl methacrylate at the same temperature. There would, therefore, seem to be little doubt that the polymerizations are free-radical in character.

All the carbonyls appear to show inhibitory action at the higher concentrations, the rate–[carbonyl]$^{1/2}$ relation departing from linearity under these conditions. Figure 1 shows a small effect of this kind for $Cr(CO)_6$

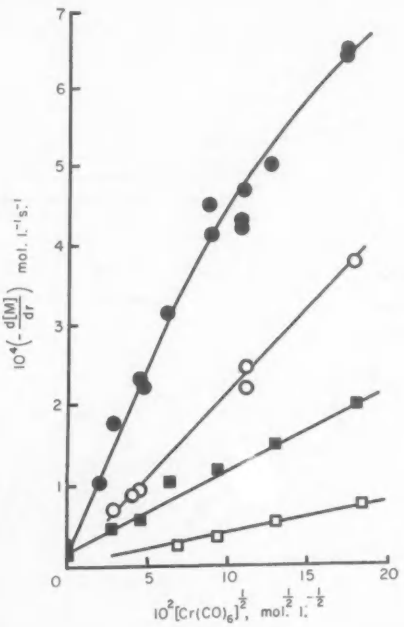


Fig. 1. Dependence of rate of polymerization of methyl methacrylate on $[Cr(CO)_6]$ at $[CCl_4]$ = 0.185 mole/l.: (●) 100°C., no CO added; (○) 100°C., 960 mm., CO added; (■) 80°C., no CO added; (□) 80°C., 915 mm., CO added.

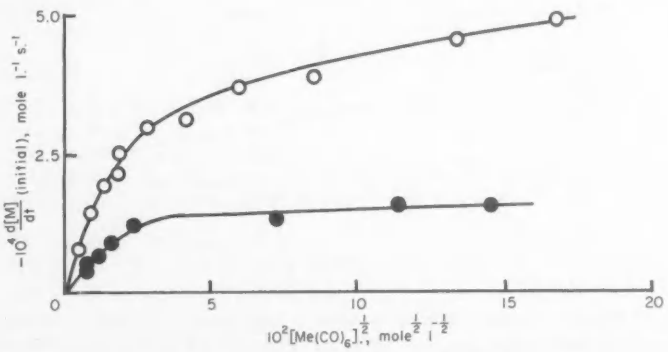


Fig. 2. Initial rate of polymerization of methyl methacrylate at 80°C. initiated by (○) $Mo(CO)_6$ and (●) $W(CO)_6$. In each case CCl_4 was present at a concentration of 0.096 mole/l. No CO was added.

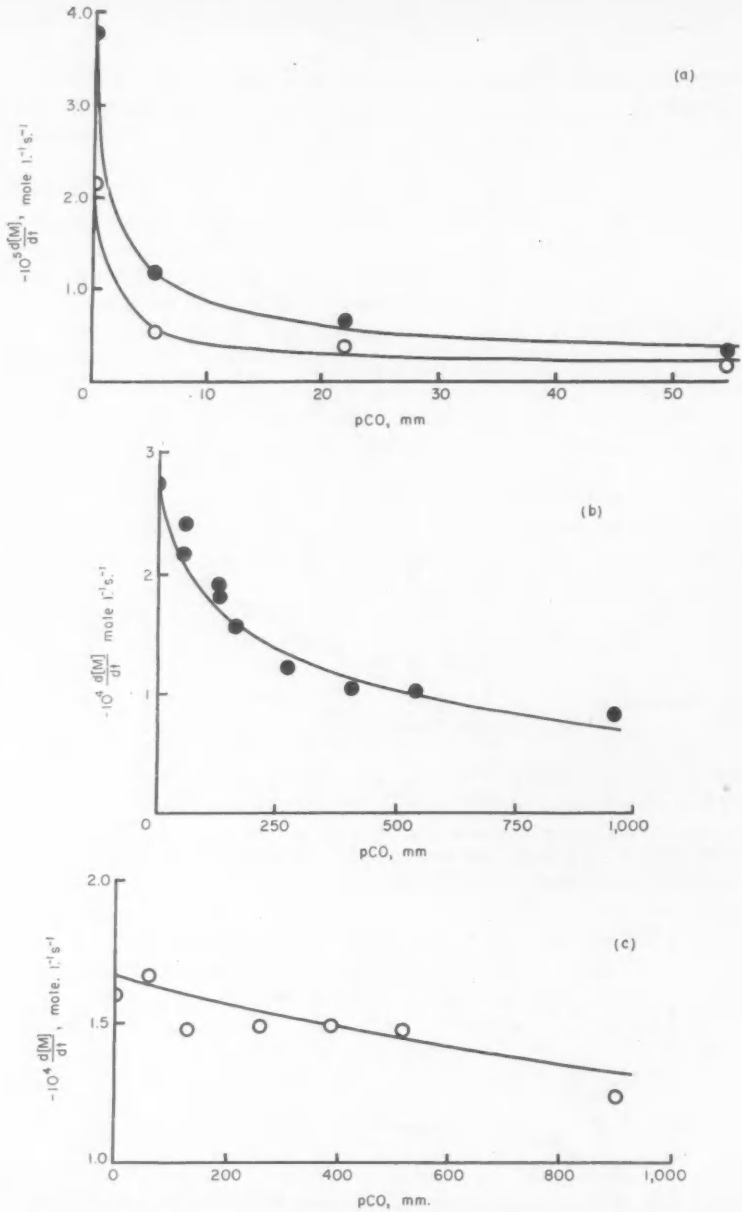


Fig. 3. Effect of carbon monoxide on rates of polymerization of methyl methacrylate nitiated by metal carbonyls. (*a*) $Ni(CO)_4$, 25°C.: (○) $[Ni(CO)_4]$ = 0.0155 mole/l., $[CCl_4]$ = 0.0105 mole/l.; (●) $[Ni(CO)_4]$ = 0.0155 mole/l., $[CCl_4]$ = 0.156 mole/l. Curves calculated[7] from equation similar to eq. (10) in form. (*b*) $Cr(CO)_6$, 100°C.: $[Cr(CO_6)]$ = 4.06 × 10^{-3} mole/l., $[CCl_4]$ = 0.046 mole/l. Curve calculated[3] from equation similar to eq. (4) in form. (*c*) $Mn_2(CO)_{10}$, 80°C.: $[Mn_2(CO)_{10}]$ = 2.37 × 10^{-3} mole/l., $[CCl_4]$ = 0.191 mole/l. Curve calculated[6] from equation similar to eq. (10) in form.

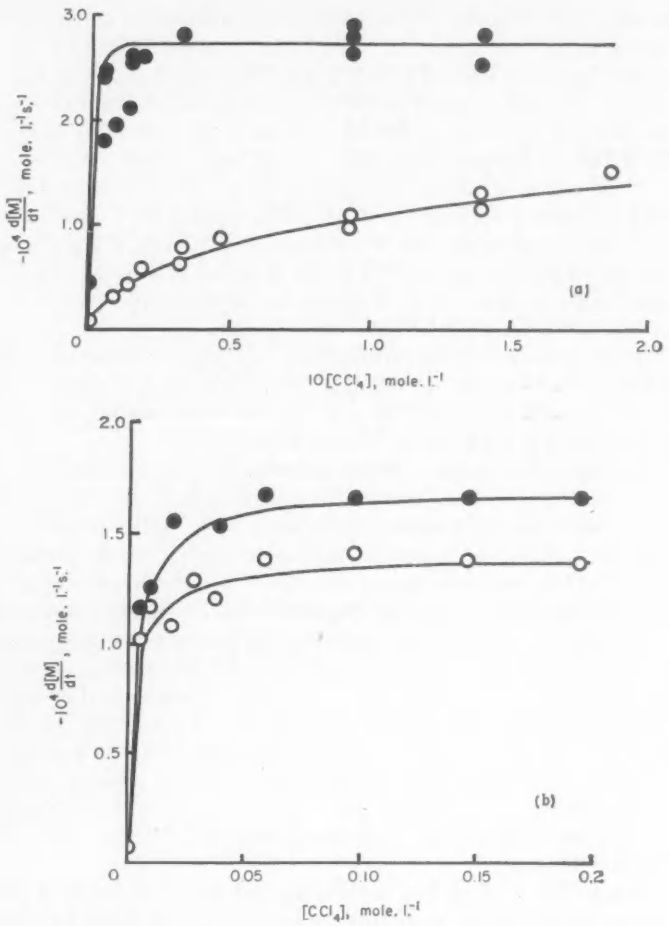


Fig. 4. Dependence of rate of polymerization of methyl methacrylate on $[CCl_4]$. (*a*) $Cr(CO)_6$, 100°C., $[Cr(CO_6)] = 4.06 \times 10^{-3}$ mole/l.: (●) no CO added; (○) 960 mm., CO added. Curves calculated[3] from equation similar to eq. (4) in form. (*b*) $Mn_2(CO)_{10}$, 80°C., $[Mn_2(CO)_{10}] = 2.37 \times 10^{-3}$ mole/l.: (●) no CO added; (○) 775 mm., CO added. Curves calculated[6] from equation similar to eq. (10) in form.

at 100°C., but inhibition is much more marked with $Mo(CO)_6$ and $W(CO)_6$ (Fig. 2). With tungsten hexacarbonyl the extent of inhibition is sufficient to make the rate of polymerization zero-order in carbonyl concentration at high values of the latter. That the effect is true inhibition and not retardation is shown by the observation that the same values of $k_p/k_t^{1/2}$ are obtained over the whole range of carbonyl concentrations. Retardation would result in a lower apparent value of the ratio. Subsidiary experi-

ments with azobisisobutyronitrile (AIBN) initiation have confirmed that the carbonyls are not retarders. Inhibition is slight with $Cr(CO)_6$ and $Mn_2(CO)_{10}$, and very marked with $W(CO)_6$, $Ni(CO)_4$, $(C_5H_5)Mn(CO)_3$, and $Co_4(CO)_{12}$. We believe that $Co_2(CO)_8$ is a very powerful inhibitor and that this accounts for the failure of this carbonyl to act as an effective catalyst.

2.22. Effect of Carbon Monoxide. In all cases which have been examined, the rate of a carbonyl-initiated polymerization is reduced by the addition of carbon monoxide. $Ni(CO)_4$–CCl_4 systems are particularly sensitive to carbon monoxide (Fig. 3*a*), a pressure of 10 mm. of the gas reducing the rate of polymerization by a factor of approximately 4. This result is remarkable; 10 mm. CO corresponds to a concentration in solution of about 1.2×10^{-4} mole/l.[3] This low concentration reduces the rate of initiation by a factor of 16, approximately. $Cr(CO)_6$–CCl_4 initiation shows moderate sensitivity (Fig. 3*b*) and $Mn_2(CO)_{10}$–CCl_4 the least degree of sensitivity to CO so far observed (Fig. 3*c*). In the latter case 900 mm. CO reduces the rate of polymerization by only about 25%.

Carbon monoxide does not behave as a retarder of polymerization. This is shown by the fact that "normal" values of $k_p/k_t^{1/2}$ are obtained in its presence, and also by control experiments with AIBN-initiated polymerizations. It is clear, therefore, that the reduction in rate produced by carbon monoxide must arise from a decrease in the rate of initiation.

2.23. Dependence of Rate of Polymerization on Halide Concentration. The dependence on halide concentration has been studied only quantitatively for systems containing CCl_4 or CBr_4. All the carbonyls give rather similar results in the absence of CO. The rate of polymerization increases rapidly with halide concentration at low values of the latter, but with increasing $[CCl_4]$ (or $[CBr_4]$) the dependence becomes less marked until eventually at sufficiently high $[CCl_4]$ further increases produce practically no change in rate. The limiting rate is generally reached for $[CCl_4] = 0.02$ mole/l., approximately (Fig. 4*a*), although with $Ni(CO)_4$ the value is rather higher than this.

In the presence of carbon monoxide, two types of behavior are encountered as the halide concentration is varied. The $Cr(CO)_6$–CCl_4 system is an example of one type (Fig. 4*a*); here, with 960 mm. CO present, the variation of rate with $[CCl_4]$ is much more gradual, the rate increasing steadily with $[CCl_4]$ over the whole range studied. On the other hand, with $Mn_2(CO)_{10}$–CCl_4 and $Ni(CO)_4$–CCl_4, the curves in the absence and presence of CO are similar (except that in the latter case the rates are lower), the increase in rate occurring over similar concentration ranges (Fig. 4*b*). The $Ni(CO)_4$–CBr_4 system is more complicated, but is essentially of the latter type.

2.3. Mechanism

The existence of a region in which the rate of polymerization is independent of the halide concentration provides a convenient starting point for a discussion of the mechanism of initiation. There appear to be two

possible explanations of such a region. First, the carbonyl and halide may form a complex with the equilibrium strongly favoring the complex, so that practically all the carbonyl is in the complexed form. (This is possible in most cases, since the halide is generally in considerable excess in the region under discussion.) If the complex subsequently entered into a radical-producing reaction (e.g., with monomer) the rate of initiation could clearly be independent of halide concentration. However, we have not been able to obtain any evidence for the rapid and extensive production of complexes between carbonyl and carbon tetrachloride under conditions similar to those holding during polymerization. Further, in the case of the $Ni(CO)_4$–CCl_4 system, the variation of the rate of polymerization with $[CCl_4]$ is similar to that found with other carbonyls, although under some conditions an excess of carbonyl is present, so that the whole of the latter could not be complexed.[7] The second type of explanation, which we favor, involves the occurrence of a reaction of the carbonyl alone, or with monomer, followed by interaction of the products with halide, yielding radicals, e.g., with $Cr(CO)_6$:

$$Cr(CO)_6 + M \underset{k_2}{\overset{k_1}{\rightleftarrows}} M \text{ - - } Cr(CO)_5 + CO \qquad (2)$$

$$\mathbf{I}$$

$$I + CCl_4 \xrightarrow{k_3} R\cdot + ? \qquad (3)$$

With sufficiently high halide concentrations the forward reaction in eq. (2) will become rate-determining. We prefer eq. (2) to a simple scission of carbon monoxide from a carbonyl molecule for reasons discussed below. The reversibility of eq. (2) would provide an explanation for the effect of carbon monoxide in reducing the rate of initiation. The simple mechanism of eqs. (2) and (3) leads to the following expression for the rate of polymerization:

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}}[M]\left\{\frac{k_1k_3[Cr(CO)_6][M][CCl_4]}{k_2[CO] + k_3[CCl_4]}\right\}^{1/2} \qquad (4)$$

A relation of this kind is consistent with the experimental observations on the Group VI carbonyls: it predicts the correct variation of the rate of polymerization with $[CCl_4]$ both in the absence and presence of carbon monoxide, and also a proportionality between rate and $[Cr(CO)_6]^{1/2}$ which is observed at low carbonyl concentrations (Figs. 1, 2, 3*b*, 4*a*). The mechanism of eqs. (2) and (3) involves a competition for the complex (I) between carbon monoxide and carbon tetrachloride; this is reflected in eq. (4) by the appearance of $[CO]$ and $[CCl_4]$ in a single term in the denominator. Clearly the greater $[CO]$, the greater will be the value of $[CCl_4]$ required to attain a given fraction of the limiting rate.

To obtain a kinetic scheme consistent with the second type of behavior mentioned in section 2.23 competition of the above type must be avoided.

This can be done formally by modifying the mechanism as shown in eqs. (5)–(9).

$$Mn_2(CO)_{10} + M \underset{k_2}{\overset{k_2}{\rightleftarrows}} I + CO \tag{5}$$

$$I \xrightarrow{k_2'} \text{inactive products} \tag{6}$$

$$I + CCl_4 \xrightarrow{k_3} II\ (+ CO) \tag{7}$$

$$II \xrightarrow{k_4} R\cdot + ? \tag{8}$$

$$II + CO \xrightarrow{k_4''} \text{inactive products}^* \tag{9}$$

Equations (5)–(9) lead to the rate expression:

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}}[M]\left\{\frac{k_1k_3k_4[Mn_2(CO)_{10}][M][CCl_4]}{(k_4 + k_4''[CO])\,(k_2' + k_3[CCl_4])}\right\}^{1/2} \tag{10}$$

if it assumed that $k_2[CO] \ll k_2'$. In eq. (10) [CO] and [CCl_4] appear in separate terms in the denominator, so that the rate–[CCl_4] relation should be of the same form in the absence and presence of carbon monoxide. This type of expression is, therefore, capable of explaining the results obtained with the $Mn_2(CO)_{10}$–CCl_4 and the $Ni(CO)_4$–CCl_4 systems (section 2.23) (Fig. 4*b*).

In the case of the $Ni(CO)_4$–CBr_4 system referred to in section 2.23 it is necessary to postulate the formation and deactivation by CO of an additional complex.[7]

Although the primary reactions involving the carbonyl [eqs. (2) and (5)] have been written as complex formation with monomer, a simple scission of CO would be consistent with the kinetic features so far discussed. Such a mechanism cannot be excluded on the basis of reported observations on the rates of exchange between the carbonyls and labeled carbon monoxide (^{14}CO).[8] With some carbonyls, e.g., $Cr(CO)_6$, $Mn_2(CO)_{10}$, the measured rates of exchange are very low; the rate of initiation required to account for the observed rate of polymerization is, however, also extremely low, and it is easy to show that with corresponding rates of scission of CO from the molecule the resulting rates of exchange would not be inconsistent with observations.[3] Several carbonyls, e.g., $Ni(CO)_4$, undergo very rapid exchange reactions with carbon monoxide. If these involve dissociation of the carbonyl molecule as the first step dissociation cannot be rate-determining in the initiation reaction at high halide concentration since it is far too rapid. In these circumstances it would appear necessary to postulate a reaction with monomer as the rate-determining step, e.g., either $Ni(CO)_4$ + M or $Ni(CO)_3$ + M.

* The rate coefficient of this reaction is written as k_4'' to agree with the notation in the original paper.[6]

It would be expected that determination of the order in [M] of the overall reaction would provide information about the nature of the rate-determining step at high halide concentrations. If eq. (2) is a correct representation of the primary reaction the order should obviously be 1.5, but if monomer does not enter into the initiation process a value of unity would be anticipated. Although the distinction is simple in principle, it is more difficult to achieve in practice, since a nonreactive diluent must be found which is a good solvent for the polymer. Comparatively few measurements of this kind have been made;[9] these have so far been restricted to $Mo(CO)_6$ and $Mn_2(CO)_{10}$. (The long Mn–Mn bond in $Mn_2(CO)_{10}$ could be a weak point in the molecule, so that the carbonyl might dissociate without intervention of monomer. Thus the two carbonyls might be expected to show extreme types of behavior.) In benzene solution the orders in [M] for $Mo(CO)_6$ and $Mn_2(CO)_{10}$ are 1.4 and 0.85, respectively. We have confirmed previous observations[10,11] that the order in [M] for the AIBN-catalyzed polymerization is unity. The low order obtained with manganese carbonyl is surprising and, since the propagation reaction alone is first-order in [M], must imply that the rate of initiation decreases as [M] increases. This could arise if interaction between the carbonyl and benzene occurs to form a complex which, on reaction with halide, yields radicals more rapidly than the complex I formed from the monomer. A similar situation with $Mo(CO)_6$ may account for the order being slightly below 1.5. It is known that benzene displaces carbon monoxide from Group VI metal carbonyls at much higher temperatures[12,13] and also that benzene is able to catalyze displacement by other ligands, e.g., diethylene glycol dimethyl ether,[13] so that these suggestions may not be implausible. The postulated interaction with monomer in the primary step (2)—a related process involving the π-electrons of the olefins—is also consistent with these observations. It should be borne in mind that the dielectric constant of benzene is less than that of methyl methacrylate and that some kinetic complication may arise from this cause.

So far we have not considered the nature of the initiating radicals. It seems almost certain that these must be Cl· or $\cdot CCl_3$, or species derived from these by addition of a single monomer molecule, arising from the reaction of I or II according to eqs. (3) or (8), respectively. A distinction between the two should be possible by using $^{14}CCl_4$; only if $\cdot CCl_3$ is the primary radical will activity be incorporated into the polymer. A similar kind of experiment could be performed by using a polymer with a high chlorine content as the halide component of the initiating system. The formation of a graft of this polymer and poly (methyl methacrylate) would show that $\cdot CCl_3$ (or the corresponding radical from the polymer) is the primary radical. Work on both these approaches is in progress at present. We may note that if it turns out that ·Cl is the primary radical, reaction between this species and CO may be postulated to account for the inhibiting effect of carbon monoxide, as an alternative to reactions (2) to (9). Chlorine atoms are known to react very rapidly with carbon monoxide[14] and might

thereby be prevented from initiating chains. Since monomer and carbon monoxide would be in competition in this case the mechanism could not account for the experimental observations with $Cr(CO)_6$, which require competition between $\cdot CCl_4$ and CO. It could, however, be consistent for the second type of behavior referred to in section 2.23, although there is at present no supporting evidence for the intervention of halogen atoms. On the other hand, the fact that different carbonyls may show very different sensitivities to carbon monoxide (section 2.22) argues against the importance of a CO–$Cl\cdot$ reaction.

2.4. Relative Activities of Carbonyls and Halides

The efficiencies of the various carbonyls as initiators at high values of $[CCl_4]$ are shown in Table III. Under these conditions we may write

$$\text{rate of initiation} = a[\text{carbonyl}]$$

and Table III gives values of a in units of 10^{-6} sec.$^{-1}$. For comparison, figures for AIBN are included. The table shows the outstanding position of $Mo(CO)_6$ among the Group VI metal carbonyls at 80°C., this carbonyl having the same order of activity as AIBN. Carbon tetrachloride is by no means the most active halide to use with this carbonyl (Table I), and values of a considerably above that for AIBN may be achieved by suitable choice of halide. The activity of manganese carbonyl is greatly reduced by introduction of a cyclopentadiene residue. At 25°C. the activity of $Co_4(CO)_{12}$ is remarkable, and we have shown that this material will initiate the polymerization of methyl methacrylate at 0°C.[15] Again, we anticipate that greater activity might be obtained with other halides.[16]

TABLE III
Rates of Initiation by Carbonyls at High $[CCl_4]$

Temperature, °C.	Initiator	$a \times 10^{-6}$, sec.$^{-1}$
80	$Cr(CO)_6$	0.42
	$Mo(CO)_6$	62
	$W(CO)_6$	9.9
	$Mn_2(CO)_{10}$	4.1
	$(C_5H_5)Mn(CO)_3$	0.17
	AIBN	150
25	$Ni(CO)_4$	2.4
	$Co_4(CO)_{12}$	1040
	AIBN	<0.1

When considering possible practical applications of these systems it is important to recall that, as already mentioned, many of the carbonyls behave as inhibitors, so that there is an upper limit to the absolute rate of initiation which may be obtained. This applies particularly to $Co_4(CO)_{12}$, which is a marked inhibitor.

At high halide concentrations the forward reactions in eqs. (2) and (5), which do not involve the halide, become rate-determining. Since the rates of radical-formation by the various halides differ greatly under these conditions[16] it follows that the radical-producing reactions (3) and (8) must be alternatives to reactions of the same species leading to nonradical products. The relative probabilities of the two types of reaction would depend on the nature of the halide, and probably on the stability of the radical derived from the latter as discussed in section 2.1.

2.5. Possible Future Developments

The investigation in greater detail of the systems we have explored in a preliminary fashion and the extension to other carbonyls and other types of metalloorganic derivatives will involve a good deal of effort, but the results of this broad field of study should provide results of chemical interest and possible practical utility. At the moment little is known of the chemistry of the component reactions and their correlation with properties of the metals and their carbonyls, e.g., the strengths of the metal–halogen bonds, or the rates of carbon monoxide exchange.[8] From the practical point of view it would be useful to have some information about the nature of the inhibition reaction. Further, it may be possible, by working in suitable solvents, to obtain significantly higher rates of initiation than those recorded in Table III (see section 2.3, discussion on order in [M]). The results with $Co_4(CO)_{12}$ lend encouragment to the idea of developing a low-temperature initiator based on these systems.

3. OTHER INITIATING SYSTEMS UTILIZING ORGANOMETALLIC COMPOUNDS

The results obtained with metal carbonyls prompted the investigation of other systems containing organometallic compounds and here we report briefly on two types.

3.1. Metal Cyclopentadienyl Derivatives

It is recorded in the literature that ferrocene is not an initiator of vinyl polymerization either alone or when mixed with benzoyl peroxide, unless the latter is already a component of a redox system.[17,18] We have confirmed that ferrocene alone is ineffective with methyl methacrylate; in the presence of CCl_4 and CBr_4, however, it becomes a definite, although weak, initiator at temperatures above 100°C. Some cyclopentadienyl vanadium and titanium derivatives have been found to behave similarly. Typical results[4] are given in Table IV.

We believe that in these systems initiation follows from an electron transfer process, ferrocene, e.g., being oxidized to the ferricinium halide:

$$(C_5H_5)_2Fe + C(Hal)_4 \rightarrow (C_5H_5)_2Fe^+Hal^- + \dot{C}(Hal)_3 \qquad (11)$$

The rate of polymerization initiated by ferrocene is not very sensitive to the concentration of the latter in the range studied and it appears that ferrocene, like the metal carbonyls, can act as an inhibitor. The molecular weights of the polymers are those to be expected in free-radical reactions proceeding at the observed rates at the state temperature, except when an active transfer agent (CBr_4) is present; $(C_5H_5)_2VCl_2$ itself appears to be a transfer agent or retarder.

TABLE IV
Initiation of Polymerization of Methyl Methacrylate (10 ml.) by Cyclopentadienyl Derivatives

Derivative	Wt., mg	Halide	Wt., g.	Temp., °C.	Conversion, %/hr.	Molecular weight $\times 10^{-5}$
—	—	—	—	100	0.5	—
$(C_5H_5)_2Fe$	80	—	—	"	0.66	—
—	—	CBr_4	0.8	"	0.94	—
$(C_5H_5)_2Fe$	5	CBr_4	0.8	"	1.86	0.32
$(C_5H_5)_2Fe$	30	CBr_4	0.8	"	2.92	0.39
$(C_5H_5)_2Fe$	80	CBr_4	0.8	"	3.28	0.29
$(C_5H_5)_2Fe$	5	CCl_4	0.33	"	2.2	—
$(C_5H_5)_2Fe$	30	CCl_4	0.33	"	1.75	38.0
$(C_5H_5)_2Fe$	80	CCl_4	0.33	"	3.1	—
$(C_5H_5)_2Fe$	5	CBr_4	0.8	120	9.28	—
$(C_5H_5)_2VCl_2$	30	—	—	100	0.0	—
$(C_5H_5)_2VCl_2$	30	CCl_4	0.8	"	3.38	0.37
$(C_5H_5)_2TiCl_2$	30	—	—	"	1.14	—
$(C_5H_5)_2TiCl_2$	30	CCl_4	0.8	"	5.34	23.4

The low activity of these cyclopentadienyl derivatives is in keeping with the observations on $(C_5H_5)Mn(CO)_3$ (Table III).

3.2. Systems Containing Metal Acetylacetonates

Metal acetylacetonates are not themselves effective initiators of the polymerization of methyl methacrylate, but in some cases they are able to initiate in the presence of halides. The following[19] are some initiating systems at 100°C.: $Co^{II}(acac)_2$ with CCl_3CN, CCl_3Br, or CBr_4; $Cu^{II}(acac)_2$ with CCl_4, CCl_3Br, CBr_4, CCl_3COONH_4. Of these, the copper acetylacetonate–ammonium trichloracetate system is outstandingly effective and we have studied it further.[20] The reactions have been carried out at 80°C.; ammonium trichloracetate alone does not initiate at this temperature at the low concentrations used.

The behavior is simplest when the acetylacetonate concentration considerably exceeds that of the salt. Under these conditions the rate of polymerization is proportional to the square root of the salt concentration, in agreement with a radical reaction. Further, the value of $k_p/k_t^{1/2}$ calculated from measurements of the rate and degree of polymerization using

(1) is also consistent with this mechanism. For purposes of illustration, when $[Cu(acac)_2] = 1.9 \times 10^{-3}$ mole/l. we have

$$-d[M]/dt = 6.3 \times 10^{-3}[CCl_3COONH_4]^{1/2} \text{ mole/l.-sec.} \quad (12)$$

(at 80°C. for $[CCl_3COONH_4] < 5 \times 10^{-4}$ mole/l.), corresponding to a rate of initiation given by 14.2×10^{-6} $[CCl_3COONH_4]$. Table III shows that this activity is rather higher than that of $W(CO)_6$.

The kinetic results are generally consistent with the formation of a 1:1 complex between the acetylacetonate and the salt, with an equilibrium constant of approximately 2700 l./mole. We have also obtained evidence for such complex formation by light absorption measurements, with an equilibrium constant close to the above value. We believe the complex is responsible for radical formation by an electron transfer of the type

$$Cu^{II} + CCl_3COO^- \rightarrow Cu^I + CCl_3CO\dot{O} \quad (13)$$

followed by

$$CCl_3CO\dot{O} \rightarrow \dot{C}Cl_3 + CO_2 \quad (14)$$

The decomposition of trichloracetyloxy radicals is known to be very rapid[21] so that the true initiating species is $\dot{C}Cl_3$. Under conditions of relatively high $[Cu(acac)_2]$ nearly all the salt is complexed, so that the rate follows eq. (12).

A kinetic complication arises from the fact that the salt is a marked retarder, interacting with growing poly (methyl methacrylate) radicals. This has been confirmed by experiments with AIBN initiation. Under conditions such that free salt is present in significant quantities the rate cannot therefore be calculated from a simple square root relation such as e.g. (12). At low total salt concentrations (e.g., 5×10^{-5} mole/l.) the rates may be calculated as a function of $[Cu(acac)_2]$ by calculating the concentration of complex using the above value of the equilibrium constant, and applying eq. (15), which is generally true for the unretarded reaction in bulk monomer at 80°C.:

$$-d[M]/dt = 7.3 \times 10^{-3}[\text{complex}]^{1/2} \text{ mole/l.-sec.} \quad (15)$$

4. STEREOREGULATION

It has been reported[22] that the presence of metal carbonyls, especially nickel carbonyl, in a system in which methyl methacrylate is undergoing radical polymerization affects the fine structure of the polymer. The isotactic component, measured by the NMR technique,[23] is increased when the carbonyl is present, mainly at the expense of the syndiotactic, the heterotactic changing little. The effect is not a large one but it seems definite. For example, at 80°C., a concentration of about 0.028 mole/l. of $Mo(CO)_6$ increases the σ value from 0.23 to 0.31. The polymer is thus made somewhat more random in character. The mechanism is not understood, but it has been suggested[20] that complex formation between the

growing chains and the carbonyl is involved. Further investigation of this matter is needed.

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Discussion

J. Corbière (*Sté. Rhodiacéta, Lyon, France*): Quelles observations avez-vois faites concernant le degré de polymerisation des produits obtenus?

C. H. Bamford: As I mentioned in the lecture, most of our work has been carried out with methyl methacrylate. The degrees of polymerization (which we have determined viscometrically) are those to be expected for a free-radical polymerization of this monomer proceeding at the observed rate at the given temperature, with only a minor contribution from chain-transfer. In other words the number-average is given by $\overline{P}_n = (k_p^2/k_t)[\mathrm{M}]^2\,(d[\mathrm{M}]/dt)^{-1}$ [cf. eq. (1) in the text of the lecture].

A few observations have been made on the polymerization of styrene initiated by $Mo(CO)_6$–CCl_4, with similar results. Preliminary observations on acrylonitrile, with the use of the same initiator, have indicated remarkably low degrees of polymerization, but I would stress that these findings require confirmation.

C. G. Overberger (*Polytechnic Institute of Brooklyn, Brooklyn, N. Y., U.S.A.*): Have you tried copolymerization of styrene and methyl methacrylate to test the free radical mechanism?

C. H. Bamford: We have not yet investigated any copolymerizations, but intend to do so. I agree this is a desirable test of the free radical mechanism.

K. F. O'Driscoll (*Villanova University, Villanova, Pa., U.S.A.*): Are these systems light-sensitive? The systems dimethylaniline–trichloroacetic acid or DMA–CCl_4 are extremely light sensitive.

C. H. Bamford: Most of the metal carbonyls have absorption bands extending at least as far as 3100 A., hence they absorb light transmitted by ordinary Pyrex glass. The systems are light-sensitive to varying extents. Dimanganese decacarbonyl, which is yellow, shows an outstanding degree of photosensitivity. The kinetic observations I have described were carried out in inactive light.

N. Shavit (*Rehovot, Israel*): I would like to report that Mr. Koenigsbuch and myself found that the system $Fe(CO)_5$ + benzoyl peroxide (BP) is a very efficient initiator for the bulk polymerization of vinyl monomers even at room temperature and lower. In the investigation of the rate of polymerization of acrylonitrile initiated by this system, we found that the rate increases with the increase of BP concentration and then decreases. The concentration of the BP at the maximum is proportional to the concentration of the $Fe(CO)_5$ employed. In each case, at relatively high BP/$Fe(CO)_5$ concentration ratios no initiation takes place at all.

C. H. Bamford: This is a very interesting result. It is possible that the $Fe(CO)_5$ in this system behaves as a reducing agent, leading to the formation of $C_6H_5COO^-$ + $C_6H_5COO\dot{}$ from benzoyl peroxide. If so, the initiation process may resemble the reaction of the halide in our systems and the polymerization will be a free radical one. The eventual decrease in the rate of polymerization with increasing benzoyl peroxide concentration may arise from a number of reasons. Thus, at high [benzoyl peroxide], ferric ion may be formed in sufficiently high concentration to retard the polymerization strongly [cf. Bamford, Jenkins, and Johnston, *Proc. Roy. Soc.* (*London*), **A239**, 214 (1957)], or alternatively, the carbonyl may be rapidly destroyed under these conditions, the initiation being only a small portion of the overall reaction destroying the carbonyl. It would be useful to have some molecular weight measurements, so that the possibilities of retardation and inhibition could be disentangled.

B. L. Erroussalimsky (*Léningrad, U.S.S.R.*): In connection with the fact of the participation of the monomer in the reaction of initiation of the free radical polymerization, I would like to mention the results of Dr. E. Milovskaya, from our Institute of High Molecular Weight Compounds (Leningrad). It is established that the initiating system $AlEt_3$ + benzoyl peroxide gives free radicals at low temperature only in the presence of monomer. In this case the kinetics of the polymerization shows all features of a free radical process. It is interesting to mention that in such a way only polar monomers polymerize (VA, MMA, AN) but not nonpolar monomers (butadiene, isoprene). The mechanism of the initiation in this system is currently being investigated

C. H. Bamford: Triethyl aluminum and benzoyl peroxide perhaps enter into a redox reaction, so that the system has analogies with that mentioned by Dr. Shavit. Dr. Erroussalimsky's observations suggest that a monomer–$AlEt_3$ complex may be the electron donor, the formation of such complexes occurring most readily with polar monomers.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1589–1600

Les Copolymères Greffés et Séquencés en Solution

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Quand on essaye de faire une revue des mémoires consacrés à ce domaine on s'aperçoit que leur nombre est vraiment très limité et que le sujet, malgré son intérêt, est loin d'être compris dans son ensemble. Il semble pourtant, que maintenant que l'on connaît assez bien les propriétés thermodynamiques et hydrodynamiques des homopolymères nous soyons arrivés au moment où il faut élucider les propriétés des copolymères; on peut donc prévoir dans les prochaines années un développement considérable des travaux dans ce domaine surtout étant donné l'intérêt pratique actuel de ce type de copolymère.

Si jusqu'à aujourd'hui peu de chercheurs ont étudié ce sujet ce n'est pas par manque d'intérêt mais surtout à cause des difficultés considérables que présente une étude de ce type. Il nous semble donc opportun avant d'essayer de passer en revue les travaux qui ont été consacrés à ce problème de montrer les problèmes que pose son étude.

Un premier problème, et peut-être le plus important, est lié à la définition des échantillons.

Si par une méthode chimique classique on essaye de préparer un copolymère greffé ou séquencé, on a en général à la fin des opérations non seulement le copolymère cherché mais encore souvent les deux homopolymères correspondants. De plus la composition et la structure des copolymères ainsi formés peuvent varier de façon considérable sans parler de leurs masses moléculaires.[1–3]

On voit donc que, alors que dans le cas des homopolymères on peut, en se plaçant dans les conditions optima, être à peu près sûr d'obtenir des chaînes linéaires ne différant que par leurs longueurs, on obtient dans le cas des copolymères en blocs ou des copolymères greffés un mélange où les espèces diffèrent par leurs masses moléculaires, leurs compositions et leurs structures. La technique du fractionnement par précipitation sélective ou par dissolution sélective qui permet d'obtenir des résultats satisfaisants dans le cas des homopolymères est donc beaucoup plus difficile dans le cas polymères séquencés.[4–6]

Devant ces difficultés il nous semble utile de diviser notre exposé en deux parties: dans une première partie nous examinerons d'abord les méthodes qui permettent de caractériser les copolymères greffés et séquencés, tandis que dans une deuxième partie nous tenterons de décrire quelques propriétés caractéristiques de ce type de substances.

I. CARACTÉRISATION DES COPOLYMÈRES

Détermination des Masses Moléculaires

On peut, lorsqu'on a affaire à un copolymère, essayer de lui appliquer les techniques classiques utilisées dans l'étude des homopolymères à savoir les mesures de tension de vapeur, diffusion de la lumière et sédimentation, et chercher la signification des résultats de ces expériences. Nous distinguerons deux cas, à savoir celui dans lequel toutes les molécules ont même composition chimique que le milieu, soit ou ne soit pas polydispersé en masse moléculaire, et celui où il y a à la fois polydispersité en masse et en composition.

L'examen un peu attentif de toutes les méthodes basées sur les propriétés colligatives des solutions où un seul résultat numérique, associé à une mesure de concentration, permet de calculer la masse moléculaire, montre que le résultat sera toujours utilisable dans le cas des copolymères. En d'autres termes il sera toujours possible d'obtenir la masse moyenne en nombre quelles que soient les fluctuations de composition du produit. Les cas de la diffusion de la lumière et celui de la sédimentation sont plus délicats et méritent un examen un peu plus attentif. Il est évident que quand le système est monodisperse en composition rien ne distingue, en principe, le copolymère de l'homopolymère. Par contre si le milieu est polydispersé soit le dn/dc soit le volume spécifique partiel dépendra de l'espèce considérée. Il faudra donc analyser les phénomènes de plus près pour voir les informations que l'on peut en tirer.

Cas de la Diffusion de la Lumière. Comme nous venons de le dire, la quantité dn/dc depend, si les indices des deux homopolymères ne sont pas identiques, de la composition x de la molécule. Si donc on applique les formules classiques de la diffusion de la lumière en considérant le système comme polydispersé il faudra écrire que la différence entre la constante de Rayleigh R de la solution et du solvant est donnée après extrapolation à concentration nulle par la formule[7]

$$\Delta R = R - R_0 = (2\pi^2/\lambda^4)n^2 \sum_i (dn/dc)_i^2 c_i M_i \qquad (1)$$

où λ est la longueur d'onde de la lumière utilisée, n l'indice de réfraction du solvant et c_i la concentration en poids du polymère d'espèce i ayant l'incrément d'indice $(dn/dc)_i$.

On pourrait penser que le fait d'avoir des $(dn/dc)_i$ différents pour les différentes molécules revient à introduire une moyenne qui ne soit plus une moyenne en poids mais une moyenne où chaque échantillon aurait un poids statistique différent.

Cependant on trouve que la moyenne ainsi trouvée dépend de l'indice du solvant. La figure 1 donne l'allure des résultats obtenus par Bushuk en portant en abscisse l'indice du solvant et en ordonnée la masse moyenne obtenue par application de la formule (1).

Le fait que quand l'indice du solvant est égal à l'indice moyen du polymère on obtienne une masse moyenne infinie, n'a rien de surprenant. En principe, à ce moment là, si le système n'était pas hétérogène en composition, aucune molécule ne devrait diffuser la lumière mais comme il y a des molécules qui ont un indice plus élevé que le solvant et d'autres qui ont un indice moins élevé, elles diffusent ce qui conduit à une masse infinie.

En admettant que l'incrément d'indice est une fonction linéaire de la composition, ce qui semble vérifié par l'expérience, on peut utiliser une autre représentation et porter M_{ap} en fonction de la quantité

$$y = (\nu_A - \nu_B)/\nu_0$$

où ν_A, ν_B et ν_0 sont respectivement l'incrément d'indice relatif au polymère A, au polymère B et au copolymère utilisé.

On obtient ainsi une parabole dont l'étude donne des indications sur la polydispersité en composition. Son équation peut se mettre sous la forme

$$M_{ap} = M_w + 2Py + Qy^2$$

où P et Q sont deux paramètres caractéristiques de la polydispersité de l'échantillon. Nous avons calculé leur valeur dans le cas d'une copolymérisation pour laquelle on obtient deux blocs et où les polydispersités des deux blocs sont indépendantes. On trouve ainsi:

$$P = x(1 - x)[M_w{}^A - M_n{}^A - (M_w{}^B - M_n{}^B)]$$

$$Q = x(1 - x)[(1 - x)M_w{}^A - M_n{}^A + x(M_w{}^B - M_n{}^B)]$$

en appelant $M_w{}^A$, $M_n{}^A$, $M_w{}^B$ et $M_n{}^B$ les masses en poids et en nombre des deux types de séquences.

Ces formules peuvent se généraliser à des systèmes plus complexes, comme cela a été montré par Leng[8] mais le résultat simple que nous venons d'exposer montre bien l'intérêt d'une étude systématique de la diffusion de la lumière en fonction de l'indice du solvant. La figure 2 montre tous les résultats que l'on peut attendre de cette étude expérimentale tandis que la

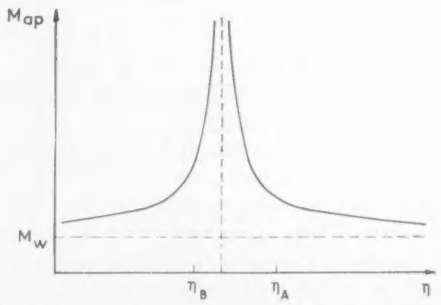

Fig. 1. Variation de la masse moléculaire apparente mesurée par diffusion de la lumière en fonction de l'indice du solvant.

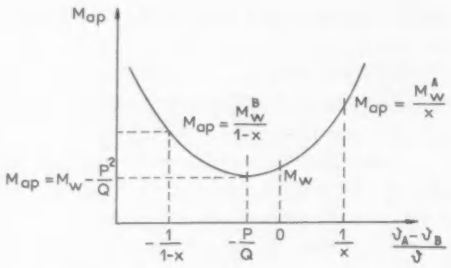

Fig. 2. Les différentes quantités que permet de déterminer la parabole des masses moléculaires.

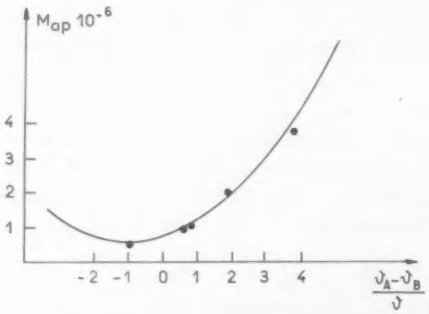

Fig. 3. Résultats expérimentaux obtenus sur un copolymère séquencé polystyrène–polyméthacrylate de méthyle.

figure 3 montre un exemple typique obtenu sur un copolymère séquencé polystyrène-polyméthacrylate de méthyle.

Cas de la Centrifugation. Si l'on se rappelle que la vitesse de sédimentation est liée à la masse moléculaire par la relation bien connue[9]

$$s = M(1 - \bar{V}\rho)(1/f)$$

où f est le coefficient de frottement, $\bar{V}$ le volume spécifique de l'échantillon et ρ la densité du solvant, on s'aperçoit que la quantité s dépendra fortement du $\bar{V}$ et de ce fait de la composition x de chaque molécule. En effet le volume spécifique du polymère peut aussi être considéré comme une fonction linéaire de la variable x. Le pic, ou la bande de sédimentation seront donc fortement élargis dans le cas d'un copolymère et il sera difficile de savoir si cet effet est dû à une large distribution des masses, ou à une large distributions des compositions. La même chose est vraie pour l'équilibre de sédimentation. La courbe d'équilibre dépend aussi de la poussée d'Archimède. Il n'existe de ce fait pratiquement aucune mesure à notre connaissance de vitesse ou d'équilibre de sédimentation effectuée sur des copolymères.

Mais comme dans le cas de la diffusion de la lumière, où on avait des effets curieux quand l'indice du solvant était égal à l'indice du polymère, on aurait aussi des effets intéressants si le poids spécifique du solvant était égal à celui du polymère. Dans ce cas en effet que va-t-il se passer? Les molécules plus riches en homopolymère léger migreront vers le haut de la cellule $(1 - \bar{V}\rho) < 0$, tandis que celles qui sont riches en polymère léger descendront au fond de la cellule $(1 - \bar{V}\rho) > 0$. Seules resteront en solution celles pour lesquelles le terme $(1 - \bar{V}\rho)$ est exactement égal à zéro.

Le procédé que je viens de décrire n'est pas très commode et par analogie avec une méthode couramment utilisée en biologie depuis les travaux de Meselson,[10] Bresler, Pyrkov et Frenkel[11] ont proposé la méthode suivante.

On choisit deux solvants, l'un plus léger, l'autre plus lourd que l'échantillon étudié, et on les mélange dans des proportions telles que le volume spécifique du mélange soit sensiblement égal à celui du polymère. Quand la centrifugeuse tourne il se forme un équilibre de sédimentation, le solvant le plus lourd descend vers le fond et de ce fait ρ est une fonction presque linéaire de la distance r à l'axe de rotation.

Supposons maintenant que l'on place un copolymère de poids spécifique donné, il se rassemblera à un niveau r_0 de la cellule pour lequel son poids spécifique est égal à celui du solvant. On a donc apparition d'une région où tout le polymère est rassemblé. On montre facilement que la répartition des concentrations est donnée dans le cas où on néglige les effets de concentration et de pression par une courbe de Gauss centrée au point d'abscisse r_0 et d'autant plus resserrée que la masse est plus grande. De façon plus précise l'écart σ^2 entre les points d'inflection est donné par la formule

$$\sigma^2 = RT/M\bar{V}(\partial\rho/\partial r)_0^{\omega^2 r_0}$$

où $\partial\rho/\partial r$ est le gradient de densité à la distance r_0 de l'axe, ω la vitesse angulaire de rotation de la centrifugeuse, v le volume spécifique du solvant et M la masse moléculaire du soluté. La détermination de σ permet donc en principe une détermination du poids moléculaire (Fig. 4).

Il faut, avant de passer au cas du copolymère, remarquer que la position exacte de la bande est souvent difficile à prévoir. En effet on a dans la cellule un système ternaire composé de deux solvants et un polymère. Du fait de l'absorption sélective le polymère peut avoir tendance à s'entourer préférentiellement de l'un des solvants ce qui modifie son volume spécifique et déplace la position de la bande.[12] Mais on voit que la détermination de r_0 permet de mesurer cette adsorption sélective dont la connaissance peut être importante pour l'élucidation des propriétés thermodynamiques du système.

Ce que je viens de dire dans le cas de l'homopolymère a fait déjà l'objet d'un certain nombre de travaux mais peu d'auteurs ont étudié le cas des copolymères. Sans s'avancer beaucoup on peut pourtant prévoir facilement ce qui se passera suivant les cas considérés.

(*a*) Supposons que l'on ait un copolymère de composition x mélangé avec les deux homopolymères parents. Pour un choix convenable de la com-

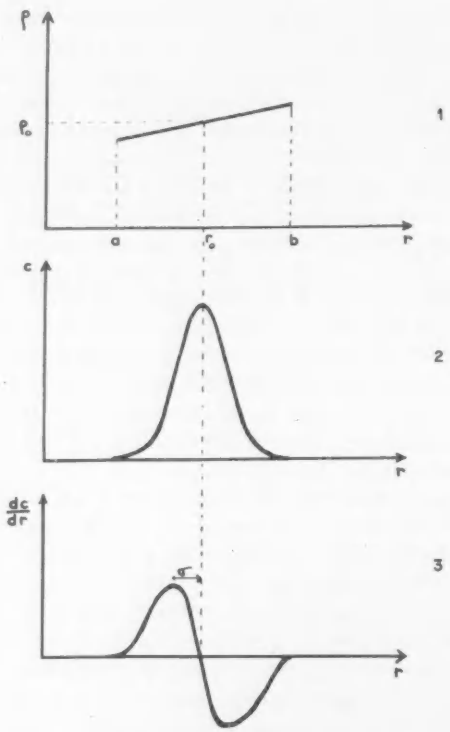

Fig. 4. Schéma des phénomènes obtenus dans une cellule de sédimentation en gradien de densité: (*1*) variation de la densité en fonction de la distance à l'axe de rotation (*2*) répartition du polymère; (*3*) répartition du gradient de concentration.

position du mélange l'un des homopolymères sédimentera au fond de la cellule, l'autre au sommet et seul le copolymére donnera lieu à un pic dont l'étude permettra de déterminer la masse, la composition, et même d'après les travaux de J. J. Hermans,[13] la polydispersité.

(*b*) Si par contre nous avons un spectra continu de compositions chaque espèce se placera, en première approximation, à l'endroit qui correspond à sa densité, et l'étude de la courbe expérimentale donnera la répartition des compositions.

Ceci est donc en principe très simple mais on se heurte à un certain nombre de difficultés dont deux nous paraissent importantes. Tout d'abord la diffusion, ou plutôt l'agitation thermique élargit le pic ce qui pour les petites masses nuit au pouvoir séparateur de la méthode. Enfin, vu les solvants organiques aisément accessibles et les vitesses de rotation que l'on peut réaliser, on n'a jamais une très grande différence de densité entre le sommet et le fond de la cellule. Cette différence porte en effet dans tous les cas concrets que nous avons pu réaliser sur quelques unités de la

deuxième décimale. On ne pourra donc pas, si l'hétérogénéité de l'échantillon est considérable et si les deux polymères parents ont des densités très différentes, obtenir en une expérience la totalité de distribution des compositions. Il faudra plusieurs expériences, et quand on sait que chacune d'entr'elles demande un assez grand nombre d'heures, on se rend compte de la lenteur du procédé.

Il faut encore adjouter que dans tout ce qui précède nous avons complètement négligé l'absorption préférentielle. Or on sait que si l'on plonge une molécule de polymère dans un mélange de solvants il se produira en général une absorption préférentielle de l'un des solvants qui changera le volume spécifique apparent de la molécule, ce qui déplacera la bande d'absorption dans la cellule. Dans le cas d'un copolymère, on peut en première approximation admettre que chacun des constituants se comporte comme si il était seul et absorbe pour son propre compte. Mais il est possible aussi que les interactions entre les différents blocs entraînent des modifications de l'adsorption et qu'ainsi des hétérogénéités de structure entraînent des différences d'adsorption sélective et de ce fait de densité.[14]

Ce fait n'a pas encore été démontré; il ne s'agit que d'une hypothèse mais il est possible que les développements de la technique d'ultracentrifugation dans les prochaines années permettent de vérifier ce point.

II. CONFIGURATION DES COPOLYMÈRES

Jusqu'à présent nous n'avons parlé que de masse et de composition, il est évident que le problème des dimensions et de la configuration des polymères greffés ou séquencès est un problème important.

Dans le cas des homopolymères, à part la flexibilité propre de la chaîne caractérisée par les empêchements stériques et les interactions à courtes distances, on caractérise l'effet du solvant par un paramètre que ce soit la quantité χ définie par Flory[15] ou le paramètre β introduit par Zimm et Stockmayer.[16] Dans le cas d'un copolymère on voit qu'il faut introduire dans un solvant unique trois quantités de ce type, par exemple χ_A, χ_B et χ_{AB} caractérisant les interactions polymère A polymère A dans le solvant considéré, les interactions polymère B polymère A ou les interactions polymère A, polymère B. On sait en particulier que les interactions polymère A polymère B conduisent en général à des répulsions ce qui a été démontré par les phénomènes d'incompatibilité.[17-19] Si en effet, on mélange dans un solvant commun deux homopolymères différents, il y a dans la plupart des cas demiction et différents auteurs ont déduit de ces expériences des valeurs du paramètre d'interaction χ_{AB}.

Quoi qu'il en soit, la notion de solvant Θ paraît inapplicable aux copolymères. En effet pour qu'un solvant soit Θ il faudrait que les trois paramètres d'interactions β soient nuls en même temps dans un solvant donné et à une température donnée ce qui paraît peu vraisemblable. De plus il peut arriver que même si l'on est très en dessous du point Θ d'une des espèces du copolymère la molécule puisse prendre une configuration qui empêche sa

précipitation. Ceci conduit à des structures entièrement nouvelles que nous étudierons plus tard. Nous allons donc passer en revue les propriétés des copolymères, d'abord dans un bon solvant, puis ensuite dans de mélanges qui jouent la rôle de précipitant pour l'une ou l'autre espèce.

Effet des Interactions sur les Configurations des Copolymères dans un Bon Solvant

Un premier point qui paraît simple consiste à chercher le rayon de giration d'une telle molécule. S'il s'agit d'un copolymère en bloc on pourrait admettre que la longueur de la chaine est égale à la somme des longueurs des blocs considérés comme isolés.

Bien que ce résultat ait été vérifié dans certains cas, on a aussi observé des écarts à cette règle, écarts qui ne sont jamais très grands, aussi n'est-on pas sûr que leur interprétation soit toujours correcte. Schlick et Levy[20] ont effectué des expériences sur des copolymères de composition et de masse déterminées dans lesquels il faisait varier le nombre de blocs. La viscosité varie indiquant que les interactions entre éléments dépendent de la structure mais il est difficile d'expliquer quantitativement leurs résultats.

De même il n'y a pas de différence appréciable entre le second coefficient de viriel d'un copolymère en blocs et d'un copolymère statistique de même masse et de même composition. La détermination de dimensions des chaînes est le plus souvent effectuée soit par mesure de la viscosité intrinsèque, soit par diffusion de la lumière. Il semble tout-à-fait logique dans le cas des bons solvants d'appliquer la théorie de Flory liant viscosité intrinsèque et rayon de giration. Le cas de la diffusion de la lumière est plus délicat: en effet si les deux homopolymères ont des indices de réfraction différents, il faudra pondérer les différents termes intervenant dans la définition du rayon de giration par les dn/dc correspondants et l'on obtiendra pour le rayon de giration l'expression suivante:

$$R_{sp}^2 = (x\nu_A/\nu)R_A^2 + [(1-x)\nu_B/\nu]R_B^2 + x(1-x)(\nu_A\nu_B/\nu^2)L^2$$

où R_A^2, R_B^2 sont les rayons de giration des parties A et B du copolymère et L^2 la distance entre les centres de gravité de A et B.[21]

Cette formule montre donc que la grandeur expérimentale ainsi déterminée ne fournit qu'une relation entre $R^2{}_A R_B^2$ et L^2 et ne permet pas de déterminer le rayon de giration vrai qui est égal à

$$R^2 = xR_A^2 + (1-x)R_B^2 + x(1-x)L^2$$

Elle montre aussi que comme ν_A et ν_B peuvent être négatifs le rayon de giration apparent peut, lui aussi, être négatif comme nous avons pu le montrer expérimentalement au laboratoire[22] (Fig. 5).

Un cas particulier intéressant de ce que peut fournir l étude de la diffusion de la lumière est celui des copolymères du type BAB étudiés dans un solvant dont l'indice est égal à celui de l'homopolymère B. On mesure ainsi le rayon de giration R_A^2 et on peut observer ses modifications sous l'effet de la presence de B.

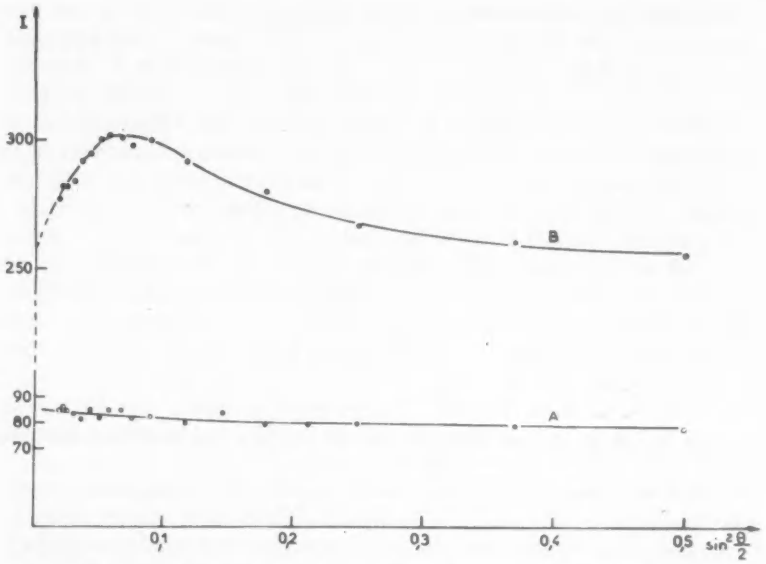

Fig. 5. Intensité diffusée en fonction de l'angle d'observation: (*A*) homopolymère en solution dans le styrolene; (*B*) copolymère séquencé en solution dans le même solvant.

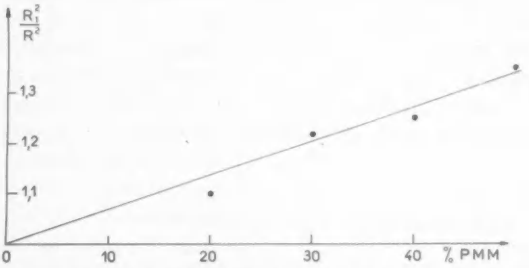

Fig. 6. Variation du rayon de giration de la partie polystyrène d'un copolymère séquencé (polyméthacrylate de méthyle–polystyrène–polyméthacrylate de méthyle) en fonction du taux de polyméthacrylate de méthyle.

La figure 6 reproduit des résultats obtenus en fixant sur les extrémités d'une chaîne de polystyrène de masse 290.000 des proportions croissantes de polyméthacrylate de méthyle.[23] On constate une augmentation très nette du rayon de giration. L'effet de volume, c'est-à-dire l'existence de contacts, entraînerait dans le cas d'un homopolymère un accroissement du rayon de giration de cet ordre. Ce résultat est donc qualitativement satisfaisant mais montre que les interactions énergétiques entre chaînons de natures différentes n'introduisent pas des interactions énergétiques très fortes.

Biréfringence d'Écoulement. Tout récemment Tsvetkov et ses collaborateurs[24] ont étudié la biréfringence d'écoulement d'un polymère formé par greffage de polystyrène sur le polyméthacrylate de méthyle. Cet échantillon était composé de 90% en poids de masse P.M.M. 600.000 et portait des greffons de masse environ 7.000. Pour éliminer la biréfringence de forme Tsvetkov utilise le bromoforme comme solvant et trouve des résultats assez surprenants. L'anisotropie optique est de signe contraire à celle du polystyrène malgré la forte proportion de ce dernier. Elle a pour valeurs 870×10^{-25} alors que pour le polystyrène elle n'est que de -140×10^{-25} et de l'ordre de 10×10^{-25} pour le polyméthacrylate de méthyle. Ce résultat est difficilement expliquable si l'on admet une structure en pelote statistique et aussi Tsvetkov et ses collaborateurs ont-ils proposé un certain nombre de modèles qui, avant d'être considérés comme valables, devront être vérifiés par d'autres expériences.

Cas où le Solvant est un Mauvais Solvant de l'Un des Deux Constituants

Il semble que cela soit pour ce type de solvant ou de mélange de solvants que les effets les plus intéressants aient été obtenus et que ce soient les propriétés de ce type de solutions qui caractérisent le mieux les copolymères séquencés ou greffés.[25]

Considérons en effet un copolymère greffé et supposons que l'on introduise un précipitant du squelette. Les attractions polymère–polymère dans ce mauvais solvant vont conduire à la formation d'une petite particule de gel quand on arrive à une composition du milieu où cette partie du polymère est insoluble. Il devrait normalement se former des agrégats, chaque fois que deux particules se rencontrent et le polymère devrait précipiter. Cependant si les greffons sont assex nombreux et si pour eux le solvant est un bon solvant, ils formeront une espèce de couche protectrice autour du microgel ce qui maintiendra la particule en solution.

On comprend bien que dans ces conditions on ait une chute brutale de la viscosité et qu'il soit impossible d'appliquer la formule de Flory relative à la viscosité. Ensuite on voit aussi que le point de précipitation d'un polymère de cette structure peut être très différent de celui d'un copolymère statistique où cet effet protecteur ne peut pas se réaliser.[26] Ceci explique en particulier toutes les difficultés qui ont été rencontrées dans le fractionnement des copolymères greffés, car le paramètre structure joul un rôle considérable.

Le schéma que je viens de proposer n'est valable que dans le cas d'un polymère fortement greffé. Quand on a affair à un copolymère séquencé portant un petit nombre de séquences, l'effet protecteur est moins grand et il peut arriver qu'il y ait assemblages de plusieurs molécules conduisant à la formation d'une micelle plurimoléculaire.[27]

On observe donc quand on augmente la concentration en précipitant, avant la séparation en deux phases, une augmentation de la masse moléculaire, liée à la présence de telles micelles qui sont d'ailleurs plus ou moins

stables. Notons d'ailleurs que ces micelles peuvent atteindre des tailles et une anisotropie considérables puisqu'ilest possible dans certains cas de les orienter par effet Kerr et d'obtenir dans des champs faibles une biréfringence très élevée.

Il semble donc que dans certains cas, les solutions de copolymères greffés ou séquencés puissent être comparées aux solutions de savon qui elles aussi forment des micelles.

Cette analogie est encore plus frappant si l'on se rappelle les résultats obtenus par Skoulios, Rempp, Sadron[28] et leurs collaborateurs sur les solutions concentrées de polymères séquencés, qui forment des gels mésomorphes où l'on rencontre des structures en feuillets et en cylindres comme dans les savons.

On est donc en présence d'un nouvel état, à savoir de solutions polymériques micellaires et un certain nombre de travaux sont en cours au laboratoire pour préciser les conditions d'obtention de ces micelles et leur domaine de stabilité.

Pour que cet exposé soit complet il faudrait aussi parler des équilibres de phase qui ont été très étudiés dans le but de préciser l'efficacité du fractionnement et de mettre en évidence l'influence de la structure sur le point de précipitation. Quelques exemples que nous venons de donner sur la possibilité de formation de micelles montrent que le problème est loin d'être simple car un polymère très ramifié peut être maintenu en solution dans un mélange précipitant l'une de ses séquences. Il n'y a pour l'instant aucun résultat général. Chaque cas est un cas particulier. Malgré les nombreux articles qui ont été publiés dans ce domaine aucun n'est assez complet pour pouvoir servir de norme pour des études ultérieures. De plus il peut arriver qu'un fractionnement augmente l'hétérogénéite de l'échantillon quand on a entre les molécules en solution des différences de structure importantes. Enfin un copolymère séquencé peut augmenter la solubilité des homopolymères en solution.

CONCLUSION

Nous venons de passer en revue les problèmes que pose l'étude des copolymères greffés et séquencés en solution. Cet exposé, a sans dout été très superficiel car j'ai systématiquement évité tous les calculs, estimant que pour une première étude du sujet il valait mieux se borner à l'aspect qualitatif des phénomènes.

J'espère cependant avoir pu mettre en évidence le comportement assez anormal de ce type de polymère et avoir pu montrer que ce domaine d'étude était juste au début de ses développements et nécessitait encore un grand nombre de travaux avant que soient bien comprises toutes les propriétés curieuses et spéciales de ces systèmes.

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JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1601–1632

Solid-State Properties of Graft Copolymers

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From the time when graft polymerization was first discovered, many investigators have studied various approaches to these very interesting systems. However, the understanding of the field remained rather obscure until recently because little attention was paid to examination of properties of such substances, especially in their relation to composition and structure. The reasons for this seem to have arisen from difficulties encountered in obtaining pure graft copolymers without homopolymer contaminations; another factor has been the desirability of obtaining in the minimum polymers of practical importance. In the present report I shall consider data on the structure and properties of graft copolymers obtained during the last few years mostly at Moscow University in collaboration with N. A. Platé, V. P. Shibaev, and others.

First of all we tried to find out how the properties of the graft copolymer are related to those of their component homopolymers—whether they are additive or somewhat of an average, whether it is possible to distinguish separately the properties of parent polymers, or whether graft polymerization results in a completely new set of properties. It seemed that the solution of the problem could be most easily arrived at by studying graft copolymers from components with very different properties. This prompted the choice of graft copolymers of starch with styrene[1] and methyl methacrylate[2] or of polyvinyl alcohol and polyacrylic acid with styrene.[3] Graft polymerization onto starch and amylose was accomplished by ozonolysis and subsequent polymerization of monomers.[1,2] Graft copolymers of styrene with polyvinyl alcohol and polyacrylic acid were obtained by a mechanochemical method.[3] In these cases the graft copolymers could be readily obtained free from homopolymer contamination because of the marked difference in their properties and particularly because of the absence of common solvents.

A thermomechanical method was generally used for evaluating the mechanical properties.[4] The method consists in measuring the deformation of a polymer material sample under a constant force applied for a given time. The temperature range was generally taken from the glassy state up to the temperature of fluidity or of thermal decomposition. The thermomechanical curves obtained can serve to characterize a polymer very generally and simply.

Deformations of starch–styrene copolymers of component ratios 40:60 30:70, and 15:85 are plotted versus temperature in Figure 1.[1] The curves

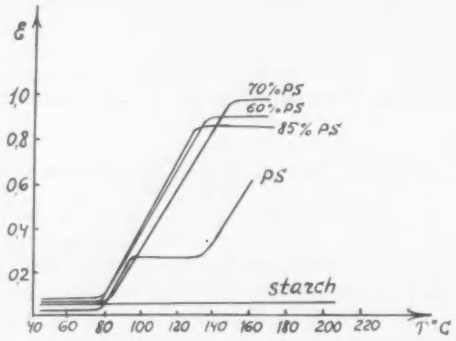

Fig. 1. Dependence on temperature of deformation of starch–styrene graft copolymers.

for pure starch and polystyrene of the same molecular weight as the copolymer are given for comparison.

One can at once observe the fact, that the glass transition for all of the samples is very close to that of pure polystyrene. All the samples soften at the polystyrene second-order transition temperature and exhibit highly elastic properties up to the thermal decomposition temperature. At the same time, even at 15% starch content, the graft copolymers exhibit no fluidity.

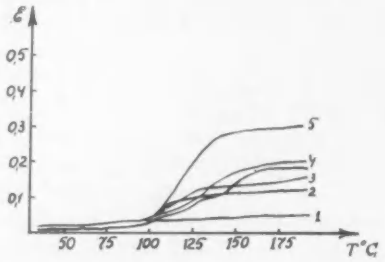

Fig. 2. Dependence on temperature of deformation of amylose–methyl methacrylate and starch–methyl methacrylate graft copolymers: (*1*) starch; (*2*) starch copolymer with 80% PMMA; (*3*) PMMA; (*4*) starch copolymer with 88% PMMA; (*5*) copolymer of amylose with 80% PMMA.

Rather different behavior is characteristic of starch– and amylose–methyl methacrylate graft copolymers[2] (Fig. 2). The softening temperatures for graft copolymers are practically the same as that for pure polymethyl methacrylate, the latter exhibiting a lower glass transition temperature. A broad region of high elasticity appears between the glass transition point and the thermal decomposition temperature. Another example is given in Figure 3 which demonstrates an analogous behavior for graft copolymers of polyvinyl alcohol and styrene.[5]

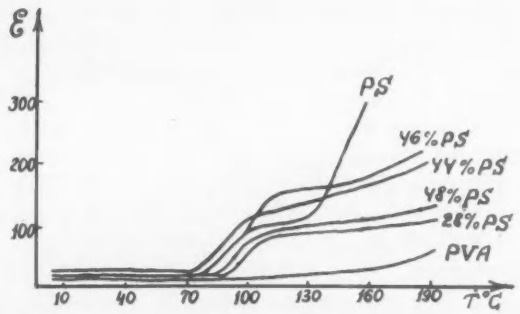

Fig. 3. Dependence on temperature of deformation of polyvinyl alcohol–polystyrene graft copolymers.

The three types of graft copolymers considered exemplify systems composed of components differing sharply different in their properties, one of the components being soluble in water and the other in hydrocarbons. This means that the component polymers of the graft copolymer are completely insoluble in each other and the homogeneity of the system is maintained only by chemical bonds between the two types of polymer chains. This leads to the conclusion that the two components must tend to separate, and any structural process must result first of all in an inhomogeneity of the system giving rise to a very peculiar phenomenon of microseparation. It can be supposed, that the observed retention of the component properties is mainly due to this microseparation process. It seemed, of course, very interesting to investigate the limits of this additivity by changing the component properties over as wide a region as possible. This could be done most easily by addition of low molecular weight plasticizers which are known to change specifically the glass transition temperature and the elastic properties of both components of the graft copolymer over a very broad region.[5]

Thermomechanical curves, shown in Figure 4, illustrate the properties of the polyvinyl alcohol–styrene (52:48) graft copolymer in the presence of tetralin as a plasticizer. Tetralin is an effective plasticizer for polystyrene, and the decrease of the glass transition temperature is directly proportional to the amount of it added (by volume). Tetralin at the same time brings about no plasticization of polyvinyl alcohol. As can be seen in Figure 4, addition of tetralin to the graft copolymer results in a decrease of the glass transition temperature just as with pure polystyrene. The glass transition temperature is plotted in Figure 5 as a function of the volume of tetralin added, as calculated for the amount of pure polystyrene present in the graft copolymer. The dependence is expressed by a straight line and is very close to that obtained with pure styrene. Addition of glycerol (Fig. 6), which is a plasticizer only for the polyvinyl alcohol, again results in a decrease in the glass transition temperature, the latter however becoming constant on addition of one

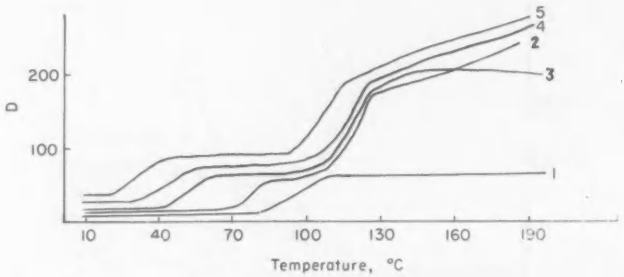

Fig. 4. Plasticization of polyvinyl alcohol–styrene (52:48) graft copolymer with tetralin: (*1*) pure copolymer; (*2*) 16% tetralin; (*3*) 20% tetralin; (*4*) 26% tetralin; (*5*) 35% tetralin.

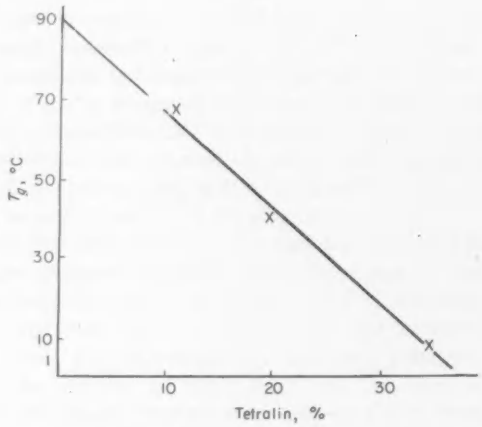

Fig. 5. Glass temperature of polyvinyl alcohol–styrene (52:48) graft copolymer vs. plasticizer (tetralin) content.

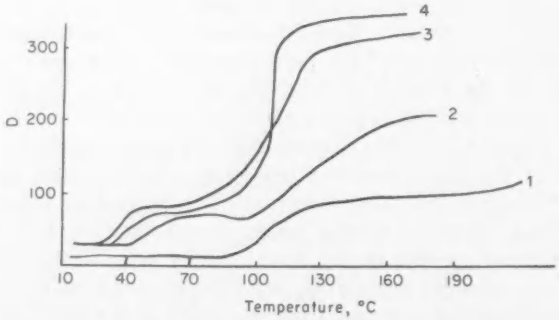

Fig. 6. Plasticization of polyvinyl alcohol–styrene (52:48) graft copolymer with glycerol: (*1*) pure copolymer; (*2*) 20% glycerol; (*3*) 25% glycerol; more than 30% glycerol.

molecule of glycerol per two polyvinyl alcohol hydroxyls. This is the maximum amount of glycerol which can be introduced into the graft copolymer. It must be mentioned that marked second inflections are seen in all of the curves; these inflections do not shift on addition of plasticizers, which probably reflects the elastic properties of the backbone polymer component not affected by the plasticizer. It is characteristic also of this type of graft copolymer that addition of only one type of plasticizer converts them to a viscous fluid.

However, both the transition points are readily shifted so as to obtain a viscous fluid by simultaneous addition of two plasticizers, specific for each of the components. The family of thermomechanical curves plotted in Figure 7 demonstrates the properties of the polyvinyl alcohol–polystyrene graft copolymer plasticized by addition of pure tetralin or glycerol or their mixtures. We can see here the gradual transition of pure copolymer (curve *1*) to a completely plasticized sample, becoming a viscous fluid already at 40°C. (curve *6*). Here it can be seen that the action of plasticizers upon the graft copolymer components proceeds independently. Quite analogous phenomena are observed with polyacrylic acid–polystyrene graft copolymers.[5]

The behavior considered above is of course characteristic only of such graft copolymers, as are composed of components sharply differing in their properties. With components whose properties differ less and less, the graft copolymers become more and more like simple mixtures of polymers. This is exemplified by the properties of graft copolymers and mixtures of nitrocellulose with polymethyl methacrylate. For these two components there is practically no difference between the glass transition temperatures of mixtures or of graft copolymers as can well be seen in Figure 8, where the glass transition temperature is plotted as function of the polymethyl acrylate content (the circles relate to the graft copolymer, the crosses relate to simple mixtures).

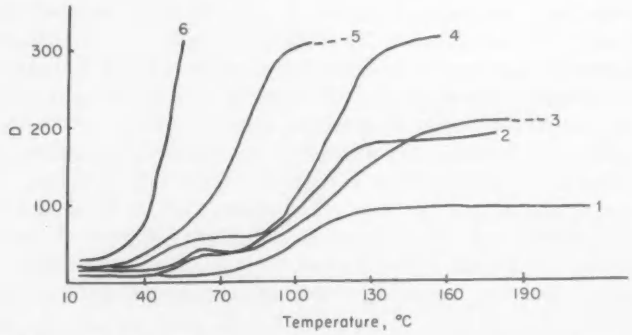

Fig. 7. Plasticization of polyvinyl alcohol–styrene (52:48) graft copolymer with tetralin and glycerol. (*1*) pure copolymer; (*2*) 20% tetralin; (*3*) 20% glycerol; (*4*) 25% glycerol; (*5*) 20% glycerol and 20% tetralin; (*6*) 25% of glycerol and 20% of tetralin.

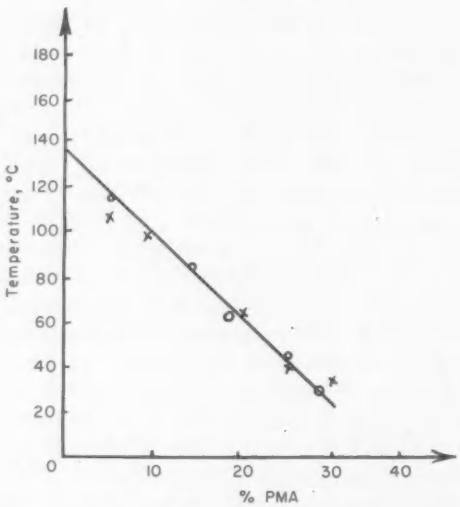

Fig. 8. Glass temperature of nitrocellulose–polymethyl acrylate system vs. content of polymethyl acrylate: (O) graft copolymer; (×) physical blend.

The general conclusion, which follows from the properties of pure and plasticized graft copolymers is the fact of retention of transition temperatures characteristic of the individual components of the graft copolymer. This fact determines the mechanical properties of graft copolymers and is of considerable practical value. The retention of transition points leads to the extension of the region of elasticity, which is the main advantage of polymeric materials.

I have discussed in the present report only thermomechanical properties, but it is obvious that other mechanical characteristics are more or less closely related to them. Ordinarily, the higher the temperature of use of a polymer material, the better are the elastic properties, and, particularly, the modulus and the impact strength. On the other hand, the higher the temperature, the lower is the tensile strength and the greater are the permanent deformations. It appears however, that it is not the transition temperatures in themselves, but the difference between the appropriate transition temperatures and the temperatures of use or investigation that is important. The greater is the difference, the better is the set of mechanical properties. This means, that by lowering the glass transition point of a given polymer we can always improve its properties (for instance, its impact strength) and by raising the temperature for the onset of viscous flow we always decrease permanent deformations and creep.

Thermomechanical curves showing the transition temperatures are the most general and convenient way to characterize the whole set of mechanical properties of a polymer. It must be well understood, that retention

of component transition temperatures in graft copolymers leads always to the expansion of the region of elasticity and first of all increases the elongations.

The above discussed relationship are best followed the greater the difference between the two polymers combined, and the smaller the opportunity for obtaining them as a homogeneous solution in the pure state. On going to similar and mutually soluble graft copolymers we observe them to exhibit properties characteristic of physical mixtures of their components. However, even for such polymers it is sometimes possible to distinguish the effects of both the components, and graft copolymers are always somewhat different in properties from common random copolymers of an analogous composition. That is, in graft copolymers their components do not lose completely their individual properties but behave to a certain extent as a physical blend. It is well known, on the other hand, that in the case of real molecular random distribution of monomer units, achieved in usual random copolymers this phenomenon is never observed. This of course leads one to think of the reasons for such an abnormal behavior of graft copolymers and of possible ways to demonstrate the microheterogeneity of the combined components.

It must be noted here, that the problem of homogeneity of polymer substances has already appeared rather long ago, in connection with the investigation of mixtures of polymer substances. It was found, that even in readily compatible polymers there can appear a microseparation, i.e., formation of regions composed mostly of one of the two polymers. The tendency of polymers to separate becomes, of course, more marked on going to components which dissolve in each other less readily, and must be very strong in graft copolymers composed of mutually insoluble components. The tendency is facilitated by the formation of intermolecular secondary structures, resulting from the association of macromolecules.

Hence, it can be anticipated, that even in case of the most equal distribution of the grafted chains one must bear in mind the possibility of the formation of regions richer in one of the components. One could expect, that the dimensions of these regions are large enough to be seen directly in the electron microscope. The first substance subjected to a structural study was the graft copolymer of isotactic and atactic polystyrenes.[6,7] This system provides an almost ideal model, both the components being identical in their chemical composition, so that the only difference consists in a different chain regularity and a greater or lesser capacity for crystallization, which serves as a basis for the graft copolymer to exhibit a special set of properties. If no crystallization takes place, the components being soluble in each other, no microseparation phenomenon will be observed, and the copolymer can be expected to behave very much like atactic polystyrene.

The graft copolymers were obtained by ozonization of isotactic polystyrene powder followed by polymerization of styrene on this peroxidized backbone polymer. The atactic polystyrene formed simultaneously was removed by treatment with methyl ethyl ketone. The thermomechanical

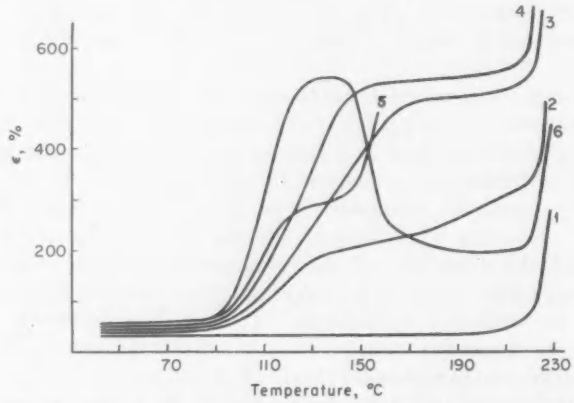

Fig. 9. Dependence on temperature of deformation of: (*1*) crystalline isotactic polystyrene (PS); (*2*) heterogeneous graft copolymer with 17% atactic PS; (*3*) heterogeneous graft copolymer with 31% atactic PS; (*4*) heterogeneous graft copolymers with 35% atactic PS; (*5*) pure atactic PS; (*6*) amorphicized isotactic PS.

curves shown in Figure 9 refer to pure components, crystalline isotactic polystyrene, amorphous atactic polystyrene, and their graft copolymers having 17, 31, and 35% atactic fraction contents. One can see here a typical picture characteristic of other graft copolymers, the glass transition point being very close to that of atactic polystyrene, and the melting point being of the order of that of crystalline polystyrene. A broad region of high elasticity is situated between the two transition points. A curve for isotactic polystyrene made amorphous by heating and rapid cooling, shown in the same figure for comparison, has a sharp maximum due to crystallization of polystyrene above the glass transition temperature. The interesting fact is the similarity of the initial part of this curve to those of the graft copolymers, the latter, however, retaining elasticity longer than the amorphous, but crystallizing sample.

Let us now consider comparative electron-microscopic structural studies of graft copolymers of isotactic and atactic polystyrenes. Isotactic polystyrene is capable of forming a complete series of intermolecular structures up to single crystals under appropriate temperature conditions. Two types of single crystals and a crystallized film of isotactic polystyrene are shown in Figure 10. Figures 11 and 12 show the structures of the graft copolymer with atactic polystyrene content ranging from 17 to 35%, obtained under analogous conditions from hot solutions or in films by prolonged heating at 140–160°C. It is demonstrated by these figures that the ability of graft copolymers to crystallize is limited by the formation of primitive forms only—from very defective crystallites up to typical fibrillar and packet structures.

It must be remembered that atactic polystyrene was grafted to the isotactic polymer after ozonization of the latter in powder form and that the

peroxide groups could appear only on the surface of the intermolecular structures of the crystalline polymer. Hence, the separation of crystalline and amorphous regions was the consequence of the method of preparation. The polymer must be considered in this case as a mixture of grafted and

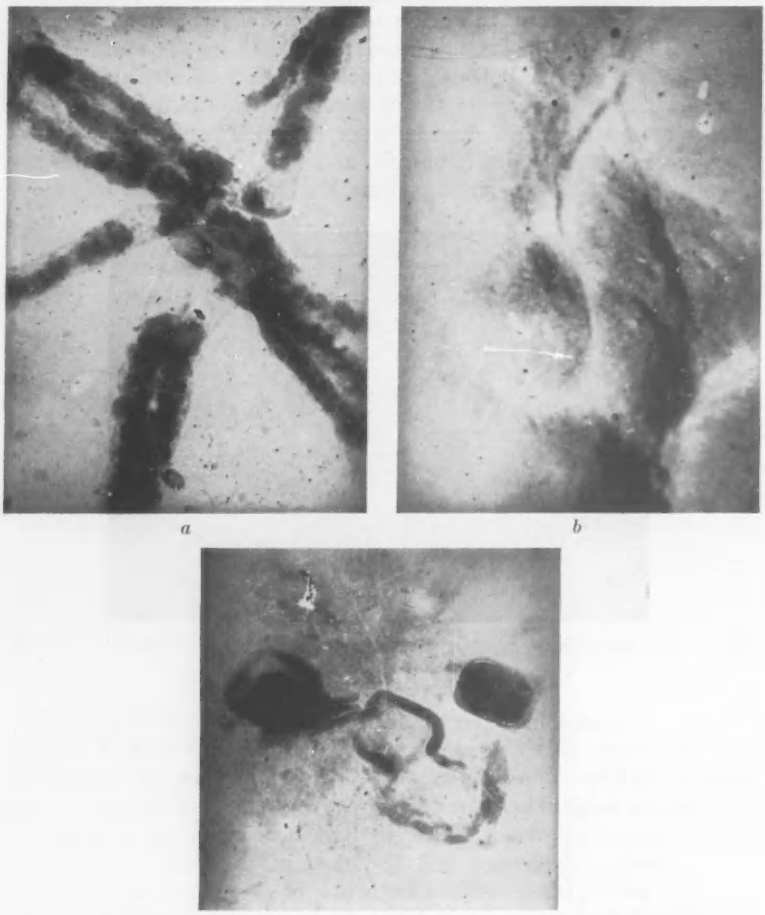

Fig. 10. Electron micrographs of isotactic polystyrene: (*a*), (*b*) from toluene solution; (*c*) from the film.

isotactic polystyrenes. However, pure graft copolymer could be isolated from this mixture. This was accomplished by complete dissolution of the substance in boiling tetralin and subsequent precipitation of the polymer with methanol. Such treatment caused complete rupture of the polymer structural system, and pure isotactic polystyrene precipitated first, the

second fraction containing graft copolymer with an isotactic polystyrene content of 25%. X-ray patterns revealed the polymer to be amorphous, though somewhat more regular than pure atactic polystyrene. Electron-microscopic study showed the graft copolymer to exhibit a typical globular structure (Fig. 13). In accordance with this, mechanical properties of the graft copolymer appeared to be close to those of the common atactic polystyrene. The thermomechanical curves plotted in Figure 14 were obtained for the isolated pure amorphous graft copolymer and ordinary atactic polystyrene. The two curves are almost superimpossible and do not differ practically from curves obtained for amorphous polymers. More detailed investigation of mechanical properties and sorption activity showed the graft copolymer to be very similar to branched atactic polystyrene.

Fig. 11. Electron micrographs of heterogeneous graft copolymer of isotactic and atactic PS from tetralin solution.

Now we can conclude, after considering isotactic and atactic polystyrene graft copolymer, that microseparation in the graft copolymer is the only basis for the latter to retain the properties of both of the two components. If crystalline zones of isotactic polystyrene are intact, a wide region of high elasticity appears between the softening temperature of one of the components (atactic polystyrene) and the melting temperature of the other (isotactic polystyrene). After destruction of crystalline zones the graft copolymer becomes very much like ordinary amorphous polystyrene, the two components in the amorphous state becoming identical. Hence, the close similarity of the two amorphous components leads to properties of the graft copolymer practically identical with those of their mechanical mixture. The difference in properties of graft copolymers and simple mixtures increases with the increasing difference between the two components, leading finally to microseparation. Grafting of two mutually insoluble components is an extreme case. This insolubility may be the consequence of differences in chemical structure, and, of the difference of polarity on the one hand and

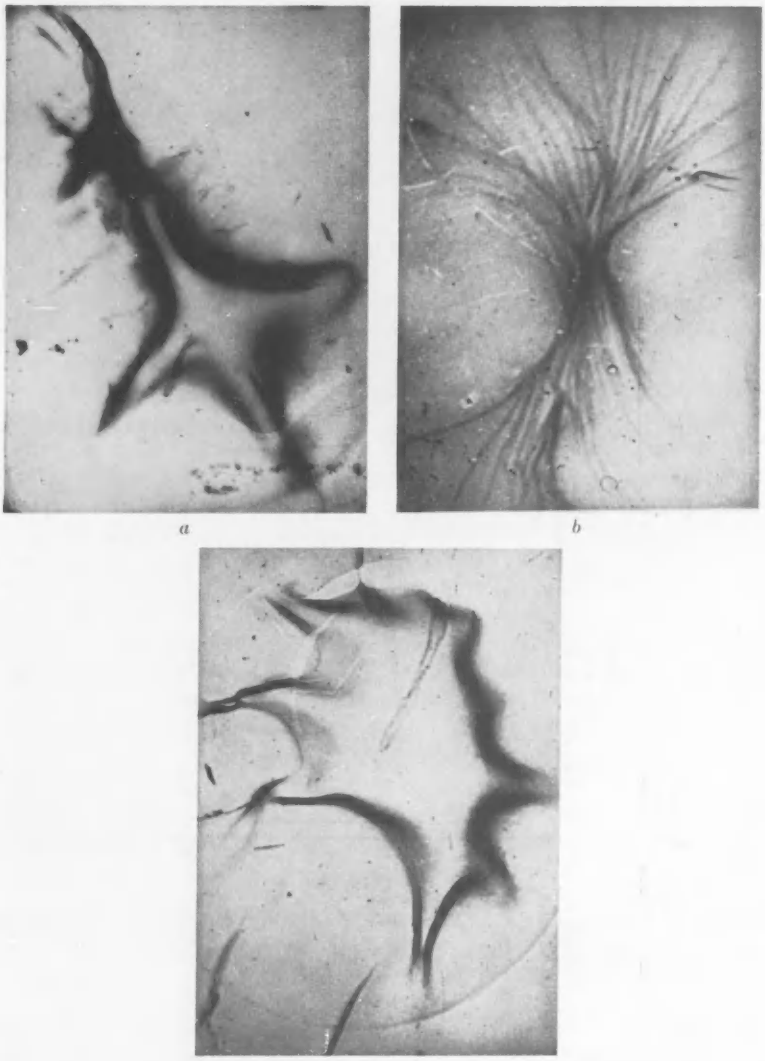

Fig. 12. Electron micrographs of heterogeneous graft copolymers of isotactic and atactic PS, from film after annealing (*a*), (*b*) at 140°C.; (*c*) at 160°C.

of the crystallization of one or of both the components on the other. Microseparation can appear in all of these cases in the equilibrium state as well, regardless of the method of preparation of the graft copolymer.

There is one more probable mechanism for the formation of separate microregions in grafted systems. Statistical distribution of the grafted

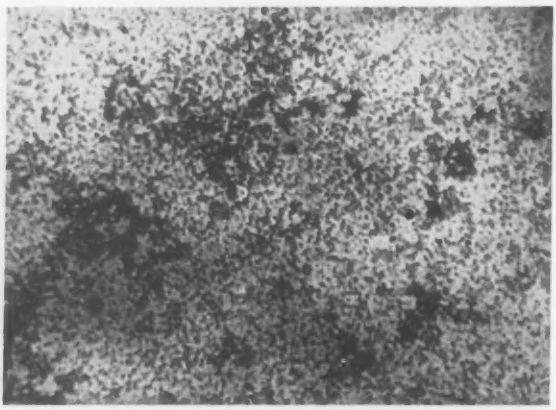

Fig. 13. Electron micrograph of molecularly grafted PS system from *o*-xylene solution.

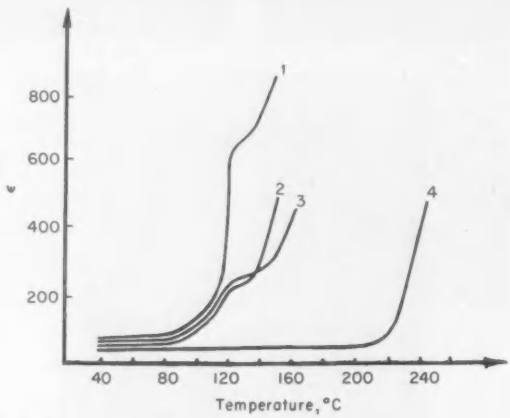

Fig. 14. Dependence on temperature of deformation of (*1*) atactic PS; (*2*) molecularly grafted copolymer with 85% atactic PS after annealing; (*3*) molecularly grafted copolymer with 85% atactic PS before annealing; (*4*) crystalline PS.

polymer molecules can take place only when the backbone polymer, the grafted monomer, and the solvent form an ideal homogeneous solution, and the rate of dissolution is much higher than that of the chemical reaction. Any secondary structures of the backbone polymer both in the solid state and in solution will allow grafting to proceed only on the surface, thus leading, from the very beginning, to structural heterogeneity of the graft copolymer. This is exemplified by the grafting of styrene to crystalline isotactic polystyrene.[7] The problem of the peculiar properties of graft copolymers thus becomes closely related to the problem of polymer structure.

The first ideas concerning polymer structure appeared as soon as it was established that polymer molecules are long chains. It seemed obvious, that no regular structures could arise from these fiberlike flexible molecules of different form and dimensions. Polymers were imagined as systems of entangled molecules with local crystallinelike regular regions, but without any separation of the crystalline and amorphous phases. It was commonly accepted, that the dimensions of "crystalline" regions (micelles) were much less than the length of the chains, which passed through a series of such micelles. The only reason for the polymers to exhibit crystalline properties seemed to be crystallization within the micelles, and the crystalline–amorphous phase ratio was considered as the major and sufficient structural characteristic. This viewpoint has not been revised by some of the investigators up to now.

The actual situation appears to be quite different from these speculations. Almost all of the crystalline polymers can form single crystals as well as large crystalline formations visible under the optical microscope or even with the naked eye. Such formations are built by a very peculiar stepwise mechanism.[8] Three years ago in Wiesbaden I had the pleasure of reporting on structures formed by amorphous polymers and of structuration phenomena preceding crystallization. A number of new substances have been investigated from this viewpoint to date, and it can now be stated, that any amorphous polymer in the solid state can form either globules, having distinct interfaces, formed by coiled macromolecules, or packets of chains, which can unite under appropriate conditions to give larger particles of (fibrils).[10] On the other hand, it now becomes obvious, that elementary structural subunits of crystalline polymers are not local regular formations of the micellar type turning continuously into amorphous phase, but that these are packet-type formations with quite distinct interfaces as in any ordinary crystal. Under the old micellar concept there was a possibility for participation of all the polymer molecules in chemical reactions, whereas the modern viewpoint obliges us first of all to consider other possibilities. The existence of intermolecular structures with distinct interfaces suggests that all the chemical processes, and, particularly, grafting, take place on the surface of these formations. On the other hand, one must start from polymers with random-type chain structure to obtain homogeneous graft copolymers. That is why it is necessary to know the precise structure of polymers in order to choose correctly the components for graft copolymerization.

It was anticipated that the most random distribution of chains would be characteristic first of all of polymers in the elastic state, i.e., in rubbers. We have recently succeeded in elucidating the structure of typical rubbers. The main difficulty encountered in this investigation arose from the surface tension of samples for electron microscopic examination. Surface tension evens the profile of the sample and makes it to turn into a droplet very much like those of viscous liquids. This phenomenon explains the failure of the first investigators to observe anything besides droplike glob-

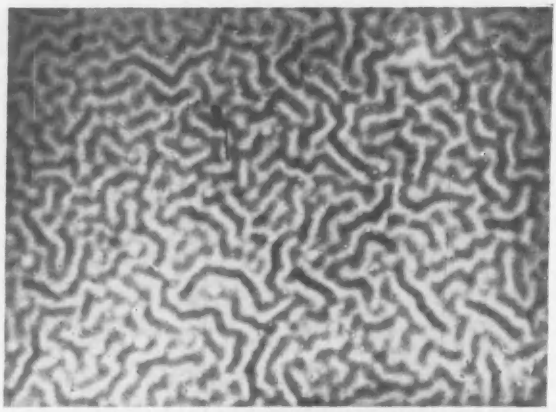

Fig. 15. Electron micrograph of irregular butadiene rubber.

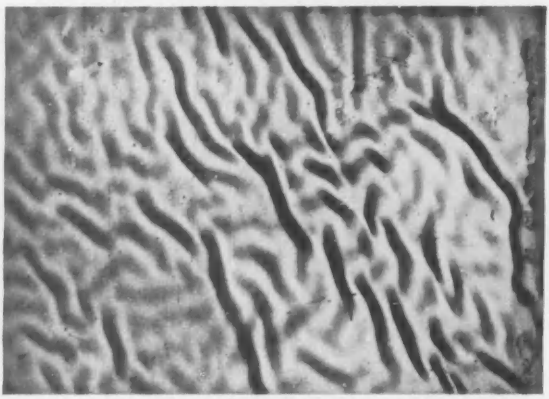

Fig. 16. Electron micrograph of random butadiene–styrene copolymer (GR-S).

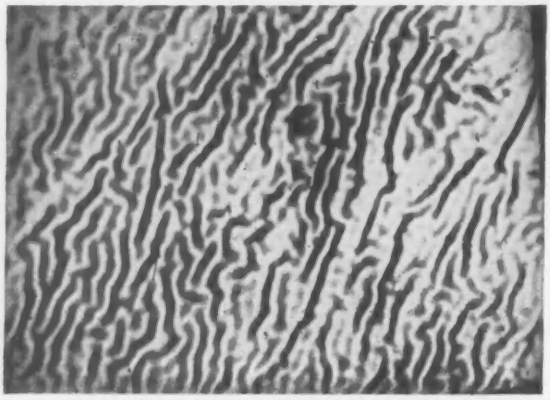

Fig. 17. Electron micrograph of natural rubber.

ules. The use of proper solvents at low temperatures enabled us to obtain preparations suitable for investigation of typical rubber structures.[11] The structure of an irregular butadiene rubber is shown in Figure 15. This structure is characteristic of all noncrystalline rubbers. The electron-microscopic pattern of a butadiene–styrene rubber is shown in Figure 16, and the electron microscopic photograph of a natural rubber preparation is shown in Figure 17. It is clearly seen in this last photograph, that strips resembling folds of a film are really rather large fibrilline formations. This is clearly seen also in Figure 18, where stretched natural rubber is shown. By heating and cooling samples of crystallizing rubbers one can observe all the gradations of the transition from the amorphous state to crystalline formations. The pattern seen on electron microscopy of an amorphous polybutene is shown in Figure 19. Besides typically large fibrils, fine packet structures of the polymer are distinctly seen. All the steps of crystallization can be followed on heating. Crystalline fibrillae of a regular

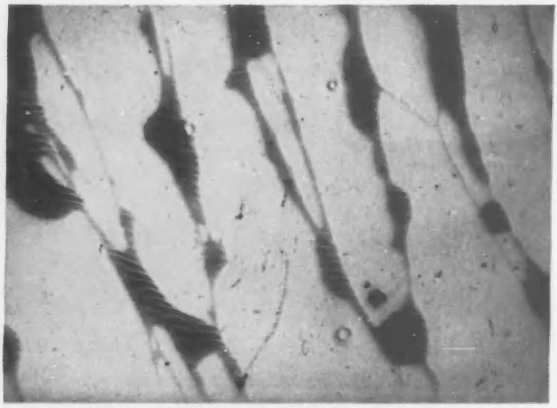

Fig. 18. Electron micrograph of stretched film of natural rubber.

Fig. 19. Amorphous poly-α-butene.

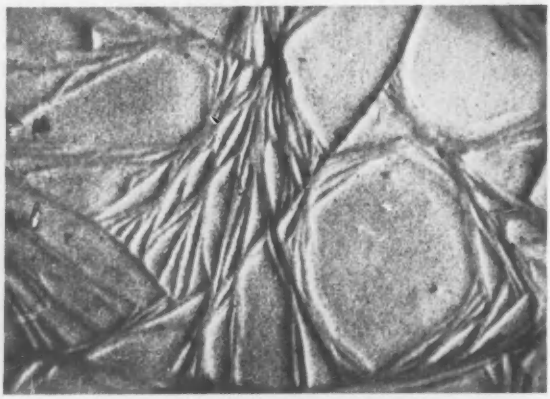

Fig. 20. Crystallizing polybutene.

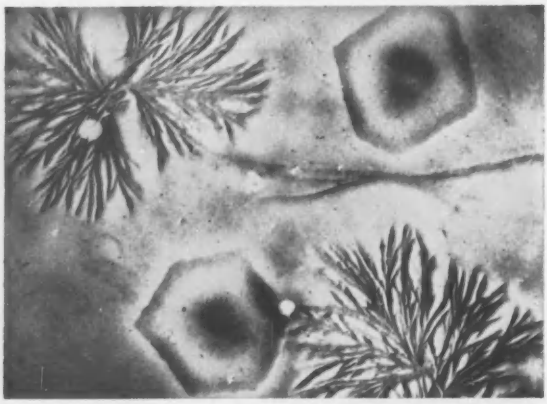

Fig. 21. Crystallizing polybutene.

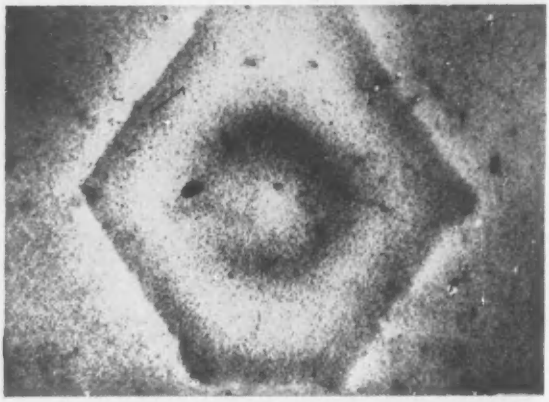

Fig. 22. Crystallizing polybutene

form are seen in Figure 20. Figure 21 shows spherulites and the initial growth of single crystals. Spherulites and separate single crystals are shown in Figure 22. Hence, even in rubbers there is a possibility for the formation of secondary structures, and it seems probable, that precise control of grafting conditions will afford graft copolymers of desired homogeneity.

However, the existence of structures in solutions and above the melting point remains rather uncertain. There is indirect evidence in favor of the existence of intermolecular structures even in molten polymers at temperatures slightly higher than the melting point. This view is supported, first, by the rapid crystallization of some polymers at temperatures higher than the glass transition temperature, and, second, by direct electron micrographic evidence revealing a regularity close to that of the crystalline state in melted polymers. It is probable, that the gradual decay of the secondary structures which are characteristic of the solid state occurs as well during dissolution as the concentration decreases and as the temperature increases.

We once had an experience showing how carefully one must evaluate the homogeneity of polymer solutions when we studied the chlorination of low pressure polyethylene with chlorine in chlorobenzene. At temperatures below 130°C. we observed the formation of a chlorinated product of a low chlorine content (2–6 times less than that of the soluble fraction), which precipitated from the solution on cooling. At higher temperature we were able to isolate only the soluble product. As we had taken all the possible precautions against any heterogeneity of the reaction mixture, it should have been the secondary structures decaying above the polyethylene melting point that were responsible for the observed heterogeneity.

Hence, it can be accepted, that grafting to intermolecular structures formed by polymer substances is a general phenomenon. An extreme case of such grafting has been reported recently by Chapiro, who studied the grafting of styrene to irradiated tetrafluoroethylene and polyacrylonitrile. The properties of the copolymers were investigated by (Endrichovskaya-Bonamour in the Sorbonne and Moscow Universities.[12] Thermomechanical curves of polystyrene–polyacrylonitrile graft copolymers (Fig. 23) showed the usual coupling of properties of the components, i.e., the retention of the glass transition temperature characteristic of pure polystyrene and the absence of melting point characteristic of polyacrylonitrile. Investigation of mechanical properties of the polystyrene grafted tetrafluoroethylene at different temperatures revealed an increase of tensile strength and a marked decrease of elongations at temperatures below the polystyrene glass transition point, both the effects disappearing at higher temperatures. It was possible to observe the heterogeneity of grafted samples microscopically (Fig. 24). Styrene was shown to be grafted to the surface of structures of tetrafluoroethylene and to polymerize partially on the interfaces. Analogous data were obtained with the polyethylene–polyacrylonitrile system.

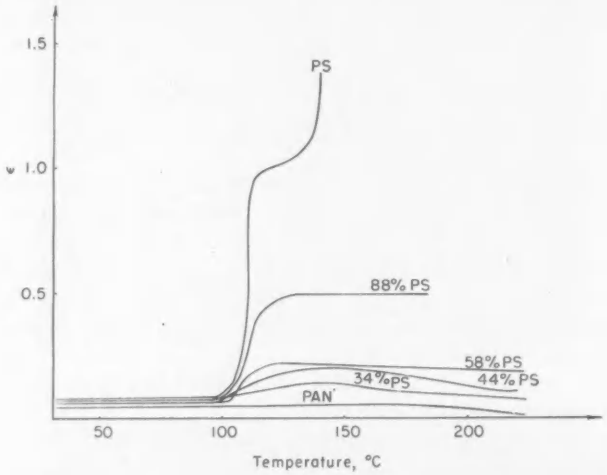

Fig. 23. Dependence on temperature of deformation of polyacrylonitrile–polystyrene graft copolymer.

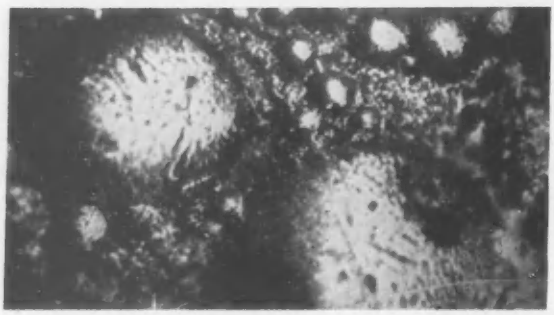

Fig. 24. Micrograph of graft copolymer of tetrafluoroethylene and styrene (optic microscope).

The examples considered are, of course, extreme cases of graft copolymerization. However, I have already mentioned while discussing the properties of isotactic and atactic polystyrene graft copolymers ps, that the decay of the initial isotactic polystyrene structure was irreversible due to grafting retarding crystallization. Grafting must always retard crystallization, as is best of all demonstrated by graft copolymers of two crystalline components. An example of such a system is provided by nylon 6–polyethylene oxide graft copolymer.

Ethylene epoxide was grafted to finely dispersed polyamide in the presence of magnesium oxide under absolutely anhydrous conditions. Thermomechanical curves for pure component graft copolymers of polyethylene oxide contents of 32, 44, and 55% are plotted in Figure 25. Two transition

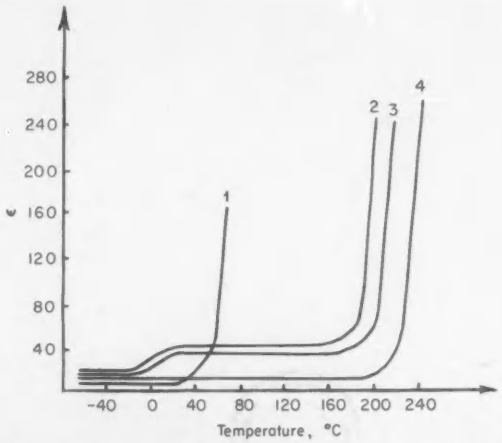

Fig. 25. Dependence on temperature of deformation of graft copolymer of nylon 6 and polyethylene oxide.

Fig. 26. Spherulites of polyethylene oxide.

temperatures are observed, the new peculiarity consisting in a continuous decrease of the pure nylon 6 melting temperature (second inflection) with increasing polyethylene oxide content. Both the components here are in theory capable of crystallization, but x-ray patterns indicate complete retention of the polyamide pattern, no additional reflections appearing after grafting the polyethylene oxide. Both the components very readily form spherulites. Polyethylene oxide and nylon 6 spherulites are shown in Figures 26 and 27, respectively. A spherulite pattern is obtained for the copolymer with 50% polyethylene oxide content (Fig. 28). The temperature of disappearance of the birefringence of the sample suggests that only nylon 6 crystallizes in this case. A mixture of the two pure components exhibits both types of spherulites with distinct interfaces, the types melting at 45 and 215°C., respectively (Fig. 29). Graft copolymer samples do not

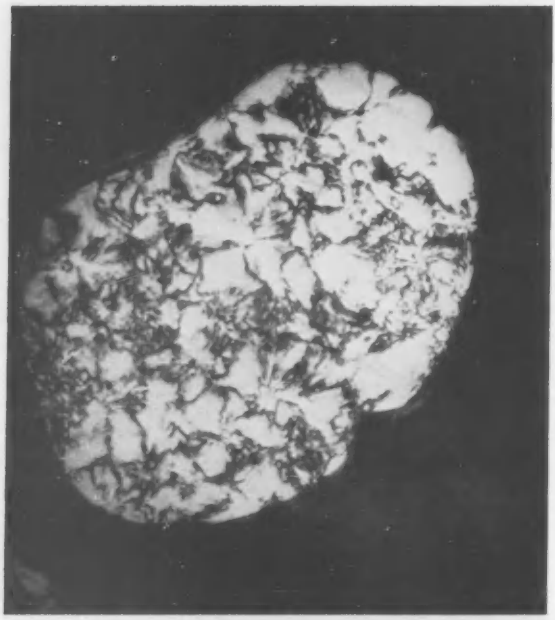

Fig. 27. Spherulites of nylon 6.

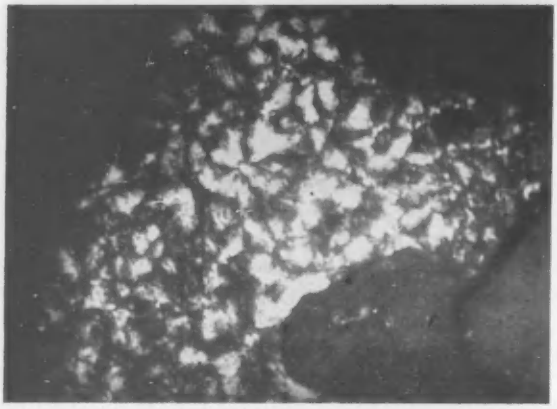

Fig. 28. Graft copolymer (50:50) of nylon 6 and polyethylene oxide (PEO).

change at 45°C., and melting begins near the temperatures of the second inflection on the thermomechanical curve. This indicates that only nylon 6 crystallization takes place, as defective spherulites of a reduced melting temperature are formed. Similar phenomena occur probably with the polycarbonate copolymer investigated by Merrill.[13]

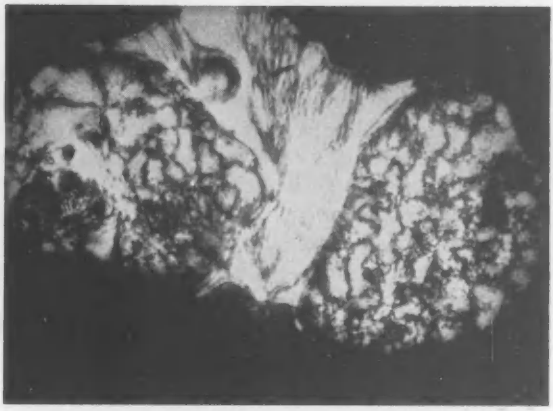

Fig. 29. Physical blend (50:50) of nylon 6 and PEO.

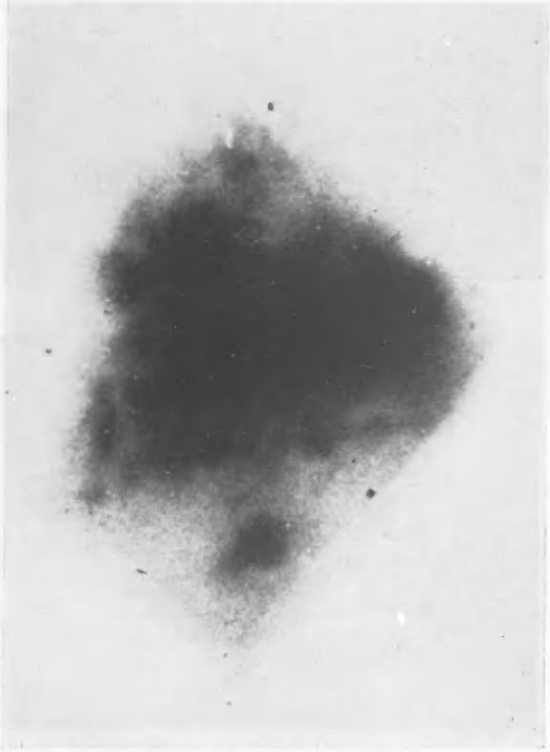

Fig. 30. Single crystal of polyoxypelargonate (POP).

Hence, the influence of grafting upon crystallization appears to be a rather interesting problem, and I shall now consider in conclusion some structuration processes, which take place during the grafting of a crystalline polymer to an amorphous one under conditions very close to homogeneity. Such an example is provided by the graft copolymer of polyoxypelargonate and polymethacrylic acid.[14] The copolymer is obtained by thermal polycondensation of hydroxypelargonic acid and subsequent addition of methacrylic acid chloride followed by the copolymerization of the unsaturated polyester with methacrylic acid in benzene solution.

Pure polyester crystallizes from solution with the formation of all possible types of crystalline forms up to single crystals (Fig. 30), and cooling of the melted polymer products large spherulites (Fig. 31). Crystallization of the graft copolymer from a good solvent (benzyl alcohol) at room tempera-

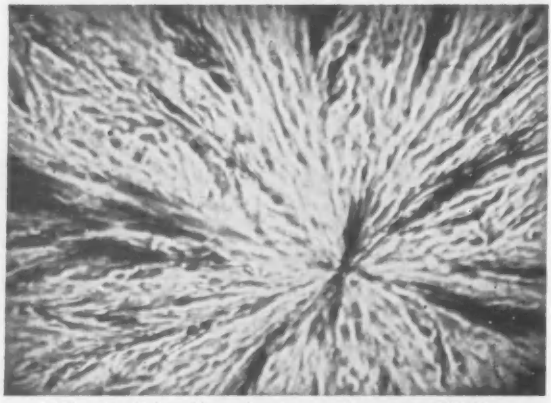

Fig. 31. Spherulites of polyoxypelargonate (POP).

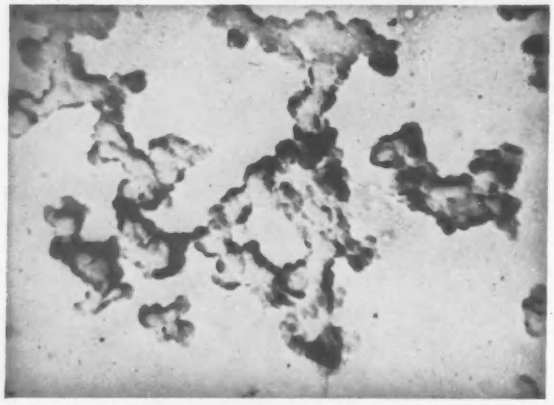

Fig. 32. Graft copolymer of polymethacrylic acid and polyoxypelargonate (50% POP) from benzyl alcohol at 20°C.

Fig. 33. Graft copolymer of polymethacrylic acid and polyoxypelargonate (50% POP) from benzyl alcohol at 60°C.

Fig. 34. Graft copolymer of polymethacrylic acid and polyoxypelargonate (50% POP) from ethanol at 60°C.

ture yielded only amorphous, though rather regular formations, when the component ratio was equal to 1:1 (Fig. 32). At elevated temperatures up to 50–65°C., i.e., near the melting point of the polyester, the conditions become kinetically favorable for microseparation (Fig. 33). If ethanol which is a good solvent for polymethacrylic acid but not for the polyester, is taken for crystallization, only typical amorphous globular structures are obtained (Fig. 34). Hence, in spite of the relatively high content of the polyester in the graft copolymer, the latter remains amorphous and capable only of forming primitive amorphous structures.

In the present report I have considered the behavior of a number of graft copolymers and tried to demonstrate the relationship between their proper-

ties and those of their individual components, from similar and mutually soluble substances to completely incompatible ones. In all of these cases one could observe the relationship between the properties of these copolymers and their structures, and, particularly, with the microseparation phenomena, caused both by the difference in chemical composition and by purely structurational processes, first of all crystallization. The role of structuration phenomena, especially in the synthesis of new grafted systems, must always be taken into consideration in research work with graft copolymers.

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Discussion

C. Job (*Sté Kléber-Colombes, Paris, France*): Je voudrais faire quelques remarques à propos de la tendance des copolymères greffés à se séparer en micro-phases distinctes, tendance dont vient de parler le Professeur Kargin.

On connait l'impossibilité thermodynamique véritable qu'ont deux polymères à former une véritable solution solide. On peut se demander, dans ces conditions, quelle est l'importance réelle de la liaison de greffage dont l'énergie est certainement faible devant l'énergie cohésive qui tend à réunir en blocs homogènes les chaînes de même nature. Ce phenomène à d'ailleurs été mis en evidence par le Prof. Banderet.

Tous les systèmes solides de ce type, que nous observons, ne sont pas dans un veritable état d'équilibre mais au contraire évoluent plus ou moins rapidement suivant les conditions imposées, vers un système à deux phases séparées.

Les descriptions morphologiques que vient de donner le Prof. Kargin sont en fait, valables pour des conditions de préparation et une histoire physico-chimique données.

Il faut rappeler, à ce sujet, les expériences de Merett qui a montré qu'un même copolymère greffé peut être myide, ou caoutchouteux suivant la manière dont sont reparties les chaînes moléculaires en phases continue et discontinue. Cet exemple montre certes les propriétés extrêmes d'un système greffé mais il souligne aussi le danger qu'il peut y avoir à determiner une propriété physico-chimique queconque sans préciser, de quelle que manére que ce soit, à quelle distance de l'équilibre veritable se trouve le système.

V. A. Kargin: I am very pleased to agree with Dr. Job's comments.

B. Seidel (*Cologne, Germany*): In his lecture Prof. Kargin showed a slide demonstrating sheaflike structures in an electron microscopic photograph of a graft polymer of atactic with isotactic polystyrene. He attributed this to microheterogeneity of the system. In work on oligomers of polyethylene terephthalate ($BzOT—[Ci—T—]_5 OBt$, where Bz = $C_6H_5—CH_2—$, Ci = $—OCH_2CH_2O—$, T = $—OC—C_6H_4—CO—$) that were completely homogeneous, we observed very similar sheaves. Would Prof. Kargin care to comment on this?

V. A. Kargin: I have not said that such structures are always attributed to inhomogeneity caused by grafting, Such sheaflike structures might be formed as one of the intermediate steps of crystallization. The grafting hinders crystallization and prevents the formation of perfect crystals (i.e., single crystals) under conditions which are favorable for perfect crystal formation in the case of the pure crystallizable polymer component.

S. H. Pinner (*B. X. Plastics, Essex, England*): The thermomechanical curves of Kargin appear to show variation in elongation as a function of temperature. Consideration of the experimental technique suggests that these curves are really plots of reciprocal apparent modulus against temperature. Nevertheless, one may question the reliance placed on the relationship between chemical constitution and shape of the curve. There is an implication that the elongation–temperature curve is smooth and uniform for homopolymer components and that deviation from the pseudo-exponential curve may be attributed to structural irregularities, also that second-order transition temperatures can be deduced.

Consideration of the actual tensile elongation of homopolymers as a function of temperatures shows that the curve may be quite complex. For example, the elongation of pure polyvinyl chloride, when plotted against temperature shows a strong peak at 100°C. and often a secondary peak at 170°C. Moreover, considerable variations can be made to the PVC by plasticization, replacement of homopolymer with vinyl chloride copolymers, addition of elastomeric impact modifiers, without changing the basic character of this curve, which is indeed very difficult to interpret theoretically. Similar curves are exhibited by other homopolymers, but with different locations of the peaks.

It is suggested that the thermomechanical technique leaves hidden some interesting aspects of the elongation of polymers at elevated temperature and that other explanations may be possible for observed deviations. Dynamic mechanical measurements as described by Dr. Wolf give more reliable information on the chemical composition of the graft copolymers.

V. A. Kargin: The tensile/elongation is not a characteristic useful for general thermomechanical study because there are a number of very different factors influencing the tensile alongation. The thermomechanical data which I demonstrated were obtained by measuring small deformations of the samples.

A. Chapiro (*Bellevue, C.N.R.S., France*): J'ái été très interessé par le résultat du Prof. Kargin selon lequel un copolymère greffé, formé de composants incompatibles et non fusibles peut atteindre un écoulement visqueux lorsqu'on lui ajoute un mélange de deux plastifiants spécifiques de l'un et l'autre polymère composants. Je voudrais poser à ce sujet deux questions: (*1*) Pensez-vous que cette observation est générale et s'applique à tous les copolymères greffés? (*2*) Pensez-vous qu'un phénomène analogue puisse se produire pour la dissolution d'un copolymère greffé dans un mélange de deux solvants specifiques de chacun des composants?

V. A. Kargin: I think that the effect of graft copolymer plastification with mixtures of the plasticizers is general and could be applied to a number of other systems. Concerning graft copolymer solutions, I have no experimental results, but I think that very interesting effects might be observed when mixtures of solvents are used.

Karl Wolf (*Badische Anilin & Soda-Fabrik A. G., Ludwigshafen am Rhein, West Germany*): If I have understood Professor Kargin correctly, he has observed that under certain conditions graft copolymers display similar mechanical behavior to heterogeneous mixtures of the homopolymers of the two components.

K. Schmieder has investigated the mechanical-thermal behavior of different types of copolymers in our laboratory with the aid of the torsion vibration method. The same results were found for graft copolymers with adequately long side chains and adequately large spacing of branching points along the main chain. The same applies to block copolymers with sufficiently long blocks.

The chairman has been kind enough to allow me to explain this by means of a few slides despite the shortage of time.

In the upper portion of all the diagrams, with the exception of Figure 3, the torsion modulus is plotted logarithmically against the temperature, and in the lower parts, the logarithmic decrement of damping (with the familiar maxima) is plotted linearly against temperature. The steps in the modulus curves and the maxima in the damping curves are related to group-motions to glass transitions, and to the melting ranges of the polymers. The nature of the relation is already known (cf. Becker and Schreuer, in *Struktur und physikalisches Verhalten der Kunststoffe*, Karl A. Wolf, Ed., Springer Verlag, Berlin/Göttingen/Heidelberg, 1962 p. 358; Heijboer, Schwarzl, and Thurn, *ibid.*, p. 363 ff.). The frequencies in the torsion vibrations were less, i.e., between 1, 3, and 10 c/s.

The modulus G' versus temperature and damping Λ versus temperature curves for a heterogeneous mixture containing equal parts by weight of poly-*n*-butyl acrylate and polyvinyl chloride have been plotted in Figure 1. Both of the polymers are amorphous. The features of both components are evident from the curves, i.e., two damping maxima and two modulus steps. In contrast to this, a random copolymer also consisting of equal parts by weight of *n*-butyl acrylate and vinyl chloride gives rise to curves with the

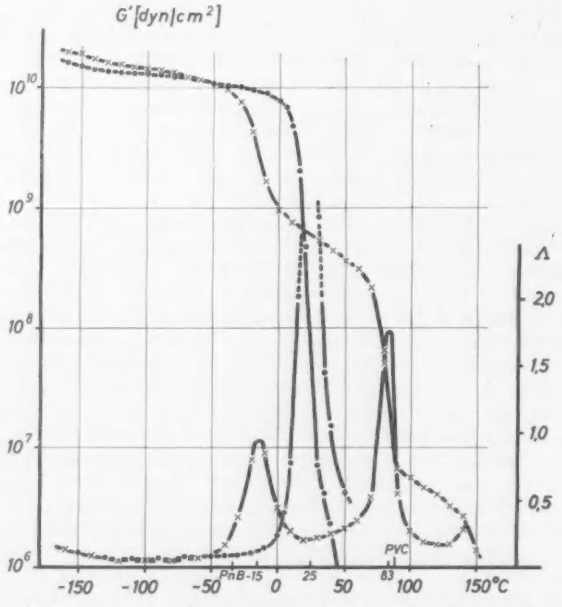

Fig. 1. G' and Λ as functions of temperature for: (×) 50/50 poly-*n*-butyl acrylate–polyvinyl chloride mixture; (●) 50/50 *n*-butyl acrylate–vinyl chloride copolymer.

one modulus step and the one damping maximum, which in this case appear at the temperature intermediate to the corresponding temperatures for the homopolymers. The same applies when two homopolymers dissolve in another or with another to form a homogeneous mixture (Schmieder, in *Strukt r und physikclisches Verhaltem der Kunststoffe*, Karl A. Wolf, Ed., Springer Verlag, Berlin, 1962, p. 791). The temperature of this damping maximum, and thus of the associated glass transition temperature, which is about 20°C. lower, is usually a linear function of the weight ratio of the two components for amorphous random copolymers. Only when the interaction between the comonomers changes in a specific manner during copolymerization is the function no longer linear. An example is amorphous vinylidene chloride–methyl acrylate copolymers, where the curve passes through a maximum.

In other cases, the curve passes through a minimum. An example of this is provided by a number of partially crystalline copolymers, whose crystallinity changes with the ratio of the monomers, e.g., passes through a minimum (K. Wolf and K. Schmieder, *Ricerca Sci. Suppl.*, **25A,** 725 (1955), Fig. 21). This effect can be ascribed to the impeding influences of the environmental crystalline ranges on the movement of amorphous segments in the chain [K. A. Wolf, *Z. Elektrochem.*, **65,** No. 7/8, 604 (1961)].

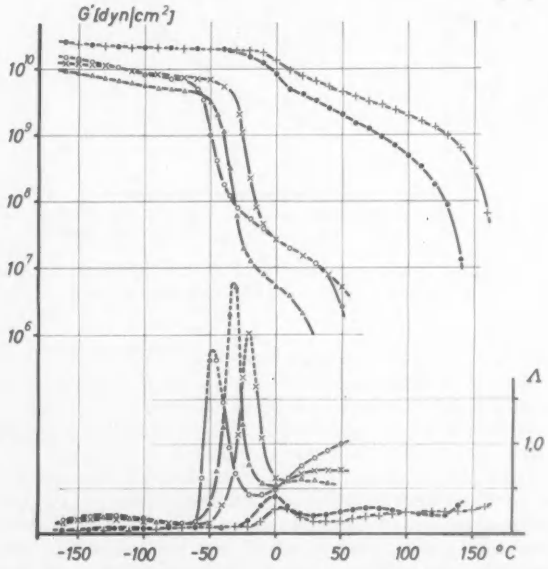

Fig. 2. G' and Λ as functions of temperature for random ethylene–propylene copolymers of various compositions: (+) pure polypropylene; (●) 5% ethylene; (×) 18% ethylene; (△) 39% ethylene; (○) 62% ethylene.

The modulus–temperature and damping–temperature curves for a few of these more or less partially crystalline random copolymers with different monomer contents, the monomers being ethylene and propylene, are shown in Figure 2. It can be seen that the damping maximum and the modulus step at +5°C. which are connected with the freezing or softening processes and thus with the glass transition temperature of the amorphous portions of the pure isotactic polypropylene, are displaced in the direction of lower temperatures as the ethylene content increases and that their intensity becomes greater until a point is reached where the ethylene content is about 40%, after which it

decreases with increasing ethylene content. This entails that the glass temperature decreases with increasing ethylene content and that the amorphous portion of the copolymer passes through a maximum at an ethylene content of about 40%. As can be seen from the shape of the modulus curves, materials with both greater and smaller ethylene contents are more crystalline. This is connected with the slope of the curve shown in Figure 3, which demonstrates the relationship of the temperatures at which the damping maxima occur to the ethylene/propylene weight ratio in the copolymer. Some points can be seen lying above the curve (×). These represent measurements made on materials with a higher crystallinity than those indicated by the fitted circles (●). As the ethylene content increases, the intensity of the maximum at about −120°C. in Figure 2 also increases. It is known that this maximum can be ascribed to the mobility of the CH_2 groups relative to the contiguous groups [K. A. Wolf, *Z. Elektrochem.*, **65**, No. 7/8, 604 (1961)].

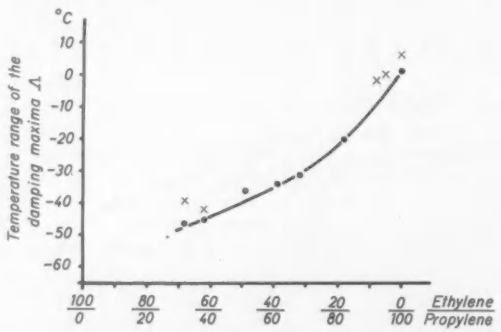

Fig. 3. Δ_{max} temperature range as a function of composition of ethylene–propylene copolymers: (×) more highly crystalline samples.

Figure 4 shows that a graft copolymer behaves quite differently. In this diagram, modulus/temperature and damping/temperature curves of two graft copolymers with a weight ratio of components of 35/65 and 45/55, the components being vinyl carbazole and branched polyethylene, are reproduced. In order to provide a comparison, curves for pure branched polyethylene, with damping maxima occurring at about −120, −20, and +55°C. and of pure polyvinyl carbazole, with a damping maximum at about 210°C., are also shown. These have been drawn in with dotted lines. It can be seen that the graft copolymer curves contain elements that are similar to those of the corresponding homopolymers of the two components. The higher the proportion of the monomer in the graft copolymer, the more pronounced the corresponding characteristic features. Thus the graft copolymers behave similarly to the heterogeneous mixtures of the homopolymers of the components. Any homopolymeric polyvinyl carbazole that may have been present in this specimen was removed by extraction.

The graft copolymers were prepared by exposing polyethylene powder to 2 m.e.v. electrons in a stream of oxygen, the dose being 4.8 Mr. and subsequently adding vinyl carbazole with the application of heat. (These specimens were prepared by D. Heinze and E. G. Kastning.) The increase in weight brought about by grafting was 52.7% for the 35/65 copolymer and 80.8% for the 45/55 copolymer. The average sizes of the blocks between two grafts were about 2000 monomers for the 35/65 and the 45/55 copolymers, assuming a G value for hydroperoxide group formation of approx. 5 (according to Dole). The average length of the side chains was 150 monomers for the 35/65 type and 220 monomers for the 45/55 type.

Figure 5 demonstrates a similar experiment in which vinyl acetate was grafted onto branched polyethylene. The vinyl acetate/ethylene ratio was 30/70. In this experiment, a compact 1 mm. thick strip of polyethylene was exposed to a dose of 9.6 Mr at a rate of 1.2 Mr/min. in the presence of monomeric vinyl acetate. As a result, the graft copolymer was not uniform: the VA content decreased from the outside to the inside. The increase in weight of the specimen was 43%. The VA homopolymer was removed by extraction. If a G value of approx. 7 for initiating the growth of the side chains is assumed, the average spacing of the grafts can be estimated at about 600 monomeric units and the average length of the graft branches at about 80 monomeric units. However, since the graft copolymerization decreases toward the center of the specimen, the length of the outside branches ought to be greater.

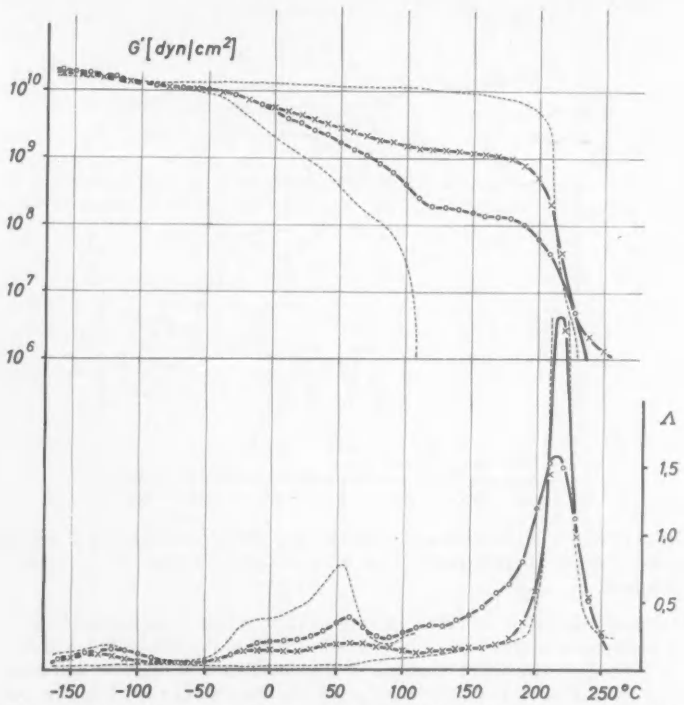

Fig. 4. G' and Λ as functions of temperature for (O) 35/65 graft copolymer of vinyl carbazole on polyethylene; (×) 45/55 graft copolymer of vinyl carbazole on polyethylene; (- -) pure polyvinyl carbazole and pure polyethylene.

The graph for pure branched polyethylene has again been shown (in dotted lines) in this figure in order to provide a comparison. Depending on the moisture content of the specimen, the damping maximum of polyvinyl acetate lies between 30 and 50°C. (absorbed water has a plasticizing action). Since the specimen was undried, the peak of the damping maximum for the graft copolymer corresponds to the position of the temperature of the moist polyvinyl acetate, whereas the portions of the damping curve decreasing in the direction of higher and lower temperatures correspond to the polyethylene curve. Thus the damping curve of the graft copolymer is similar to that obtained additively from the curves for the corresponding homopolymers of the compo-

nents. Again, the graft copolymer behaves similarly to a heterogeneous mixture of the homopolymers of the components. The curve of a random copolymer of VA and ethylene present in the same ratio, i.e., 30/70, has also been drawn in for purposes of comparison. The damping maximum occurs at a much lower temperature, i.e., at about −22°C.

Similar results to those obtained with the two graft copolymers in Figures 4 and 5 were also obtained with other graft copolymers, e.g., polyethylene–acrylonitrile, with the sole provision that the graft side chains and the blocks of the main chain were large enough.

Further experiments were made with ethylene–propylene block copolymers, specimens of which were provided by K. F. Hansen.

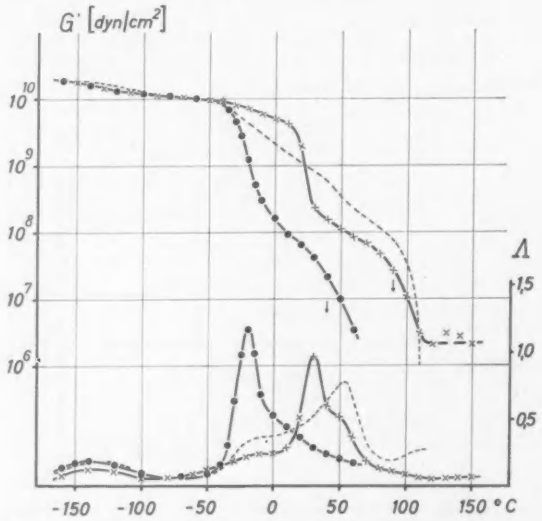

Fig. 5. G' and Λ as functions of temperature for: (●) 30/70 vinyl acetate–ethylene copolymer; (×) 30/70 graft copolymer of vinyl acetate on polyethylene; (- -) branched polyethylene.

Modulus–temperature and damping–temperature curves of an initial series of these block copolymers are reproduced in Figure 6. Each of the molecules (weight-average molecular weight about 10^6) consisted of six blocks each of ethylene and propylene. The size ratio of an ethylene block to a propylene block is not exactly known, but from the manner in which they polymerized it would appear that the sizes of the two types of block are not of widely different orders of magnitude. The polymerization was carried out in such a manner that pure undisturbed ethylene and propylene blocks are formed. This was ascertained by Gg. Schnell with the aid of infrared spectroscopic investigations. (A more detailed publication on block copolymers derived from α-olefins is being prepared by Gg. Schnell and K. Schmieder.)

The result of the torsion analysis in Figure 6 shows maxima at 5°C. which could only have been caused by the amorphous parts of pure propylene blocks. The maxima at about −120°C. are characteristic for polyethylene, as was stated above. Their intensity increases with increasing ethylene content. An increase in the amount of ethylene in the block copolymer displaces the damping curves upward to a higher level at temperature above 30°C. This agrees with the fact that the damping curve of linear polyethylene lies much higher in this temperature range than that of isotactic polypropylene.

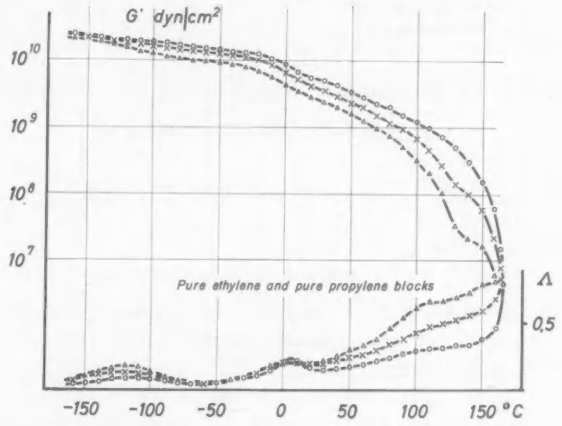

Fig. 6. G' and Λ as functions of temperature for ethylene–propylene block copolymers of various compositions: (O) 22% ethylene; (×) 42% ethylene; (Δ) 78% ethylene.

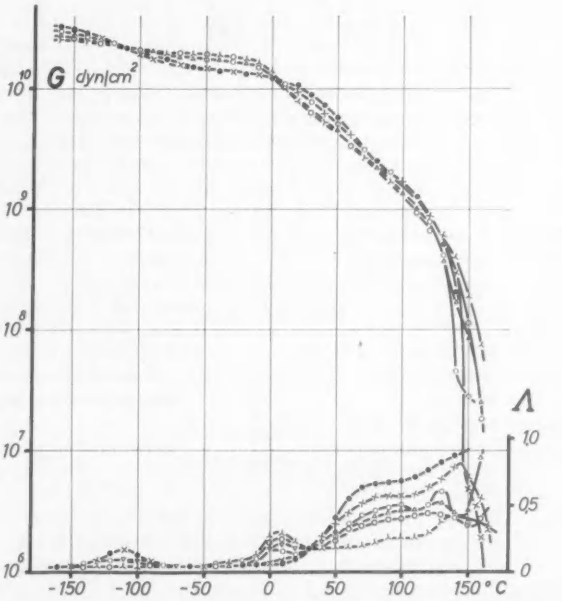

Fig. 7. G and Λ as functions of temperature for polyethylene–polypropylene blends of various compositions: (●) 100/0; (×) 80/20; (O) 60/40; (Δ) 40/60; (⬡) 20/80; (▲) 0/100.

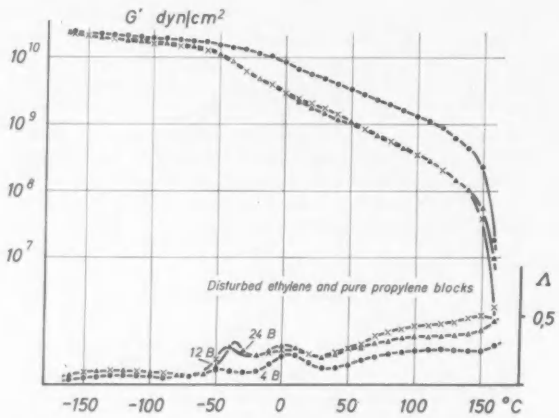

Fig. 8. G' and Δ as functions of temperature for ethylene–propylene block copolymers of various compositions: (●) 33% ethylene; (▲) 56% ethylene; (×) 68% ethylene.

This behavior and the fact that no further maximum occurs at −20°C. indicates that polyethylene blocks have a linear configuration. This conclusion is reasonable in view of the manner of polymerization. In order to provide a comparison, curves for heterogeneous polyethylene–polypropylene mixtures in various ratios are shown in Figure 7. These curves are similar to those of the pure ethylene–propylene block copolymers.

Other ethylene–propylene block copolymers, likewise containing completely pure polypropylene blocks, were prepared by K. F. Hansen. The ethylene blocks, however, were seriously disturbed by propylene, as also determined by means of infrared analyses. The number of blocks of each type per molecule in the ethylene-rich polymers was 12 and 24, and in the ethylene-poor product 4 (weight-average molecular weight also about 10^6).

Modulus and damping curves for these copolymers are shown in Figure 8. In contrast to the damping curves shown in Figures 6 and 7, new maxima occur between −30 and −50°C. Reference to Figures 2 and 3 indicates that their positions could be reasonably explained by assuming that part of the blocks consists of random copolymers of ethylene and propylene, which would cause these maxima, and that the other part of the blocks consists of pure propylene sequences, which would cause the maximum at +5°C. The maximum at −120°C. can be ascribed to the CH_2 groups of the ethylene. The behavior of the curve above 30°C. would appear to be primarily influenced by the content of crystallized ethylene sequences in the copolymer. However, the damping curves occupy a lower position than those for block copolymers with undisturbed blocks (Fig. 6), the ethylene content being the same.

The cohesion of those block copolymers, like that of graft copolymers, is governed by the components melting or softening at higher temperatures. This can be seen from the modulus curves.

To conclude, it would be reasonable to say that the mechanical-thermal behavior both graft and block copolymers that have adequately large blocks and side branches is very similar to that of heterogeneous mixtures of the corresponding homopolymers.

V. A. Kargin: The data obtained by Prof. Wolf seem to me to be very interesting, and they show again that in graft copolymers the role of each individual component is very important and brings to all systems the properties of both polymer components.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1633–1650

Structure and Electrical Properties of Some Synthetic Solid Polymers

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Electrical states in synthetic polymers are technically of the highest interest, for modern electrotechnology depends largely on the nonconducting qualities of solid plastics, fibers, and rubbers to provide insulation.

In turn, their roles as structural and insulating components have stimulated intensive study of the structure and chemistry of polymers. Macromolecules have also become interesting scientifically, especially in relation to their occurrence and functions in living matter, such as in the form of plant cellulose and animal protein and protein complexes.

New families of synthetic polymers have revealed an astonishing range of dielectric and conducting qualities,[1,2] detailed in many studies in the past two decades. Concurrently, solid-state science and engineering have brought a new wave of understanding of electrical states in crystals, especially of semimetals and metals.[3] Technical values of *p-n* junction devices, such as the transistor, the silicon rectifier, and solar photoelectric cell, have dramatized the diversity of electrical effects which are displayed in the electronic conditions lying between metal and insulator states. Then, growing interest in signal and information processing, and energy transfer mechanisms, particularly in living matter, has increasingly pointed to special features of such macromolecules as proteins and nucleic acids.[4–6] This, and similar concern about charge transfer in enzymes and other organic structures[7] also have stimulated studies of synthetic polymers. In these, chemical composition and structure can be both varied and controlled, so that simplified effects often provide analogies for more complex natural systems.

Accordingly, we shall survey the present situation, with particular emphasis on the principles which underlie primarily the direct current conductivity of some partially known polymer structures. However, we shall also remark occasionally on magnetic, and even on dielectric qualities. The class of electrical properties provided by synthetic polymer mixtures with metals, salts, and oxides will not be discussed. Also, rubbers made conducting by compounding with carbon black, plastics containing either organic or inorganic ionized adducts,[8] and even the polycoordination of chelates and polyelectrolytes themselves do not form part of the present survey, which is restricted to intrinsic electrical qualities within and between covalent synthetic macromolecules themselves.

"Structural Units" and Monomeric Analogs

Indeed, with respect to principles we shall consider in the synthetic polymer solids, it is now timely to examine expected electrical behavior of their subunits, as also represented by low molecular weight organic compounds. (This "statistical structure unit" aspect of polymers was earlier useful in elucidating their dipolar and crystal packing behavior.) A global upsurge of study in the past few years on the "semiconducting" properties of organic crystals, itself excited by extensive understanding of inorganic semiconductor crystals, has induced several significant concepts. These have been critically reviewed by Garrett and others.[9,10]

Particularly, we shall see, as pointed out earlier,[11] that the elegant advances of theory and experiments in the inorganic elemental (and simpler compound) semiconductors have sometimes caused eager efforts bodily to transfer findings from that field to the organic systems. It is beginning to seem that little if any direct equivalence exists. Let us consider the simplest electrical basis for conduction in an applied electric field as

$$1/\rho = \sigma = \mu_n q n$$

where σ represents electron conductivity in reciprocal ohm centimeters due to a number of electrons n, each having a charge q of 1.60×10^{19} coulombs, multiplied by a mobility or drift velocity of the carriers in centimeters per second, in a field of 1 v./cm., μ_n. Of course, there is an equivalent situation for other carriers such as positive holes. Generally the observed total reciprocal resistivity equals $1/\rho = \sigma = q(\mu_n n + \mu_p p)$. Accordingly, (*1*) the generation of carriers leading to populations of n and/or p in numbers and sign, and (*2*) their mobility in the solid, will be the particular factors determining polymer conductivity. But with respect to smaller molecules, at least, the formation of the observed population of charge carriers may in effect be determined just by those which can hop from center to center, or in many cases, molecule to molecule. The electronic configurations in these systems can be represented by extremely narrow bands. Although rather high drift mobility has been reported for single crystals of solid anthracene,[12,13] with μ about 1 cm.^{2}/v. sec. for both holes and electrons, general indications are that mobilities in organic systems are orders of magnitude less than this. For instance, in this and most other cases to be cited, it is impossible to observe a Hall effect.

$$R = 10^8 \, Vt/IH = \mu_H/\sigma$$

where V is voltage, I is current, H is applied magnetic field, t is thickness in centimeters, and $R \sim 0$ indicates that μ is about 10^{-3} or less.

Also, the inverse dependence of mobility on temperature suggests that the principal observed influence of temperature, to increase conductivity, is to change the effective charge carrier population. This will appear in combination with the hopping abilities in the expression

$$\sigma = \sigma_0 \, e^{-E_A/kT}$$

where σ stands for the usual conductivity and E_A represents activation energy for the hopping process. (Anthracene and various other organic compounds have also been found to show photoconductivity. Apparently, excitons produced by optical absorption do transfer through the crystal and probably exert a major effect by creating a hole electron pair at the surface.)

An interesting study with respect to synthetic polymer systems of aromatic hydrocarbons involves combinations of the fused-ring compounds tetracene, pentacene, perylene, and anthracene.[14] The activation energies vary little for the pure members, but were reduced by 20 or 30% when about 10^{-3} parts of one was added to another. In a series of recent studies, Glarum[15] constructed theoretical schemes for estimating charge mobility in such organic systems. Even in the case of anthracene, for which a puzzling high mobility has been reported, he believes that charge motion in the crystal is intermediate between hopping mechanisms and the classic wave packet travel of truly periodic semiconducting media. It is estimated that most organic molecular crystals should have maximum mobility of 10–30 cm.^{2}/v.-sec. While this treatment necessarily involves many idealizations, it is probable that only if resonant energies between molecules of around one or more electron volts exist is there departure from low charge mobility, probably representing a site-hopping movement.

The charge transfer complexes which may have conductivities as high as 100 (ohm-cm.)$^{-1}$, such as in iodine–perylene,[16] may also bear on some of the principles of certain synthetic polymers, through the high concentrations of paramagnetic electrons found in both systems. Indeed, in the perylene complex there seems to be an electron carrier present for every iodine molecule. Again, the mobilities are extremely low, being less than 10^{-2} cm.^{2}/v.-sec. Similarly, an upper limit of u of about 4×10^{-2} cm.^{2}/v.-sec. was found for the TCNQ or tetracyanoquinodimethane salts studied by Kepler and co-workers.[17] However, rather extreme variations of structure will be involved in producing configurations in synthetic polymers really close to those found in these charge complexes, in which a relatively easy thermal process apparently leads to ionization.

This is emphasized by considering the situation in, for instance, anthracene. Electron transfer succeeding by ionization would, of course, require energy equal to the difference between the ionization energy E_{ion} and the electron affinity of the molecule E_{aff}. This is about 6 e.v., whereas the activation energy for conduction in the dark in anthracene is something like 1 e.v. This is just another way of emphasizing present indications regarding conduction behavior of organic systems. Particularly in polymers, there is not a blending of ground molecular states resembling the valence band in an elementary semiconductor. Even less do we see triplet molecular states corresponding to a normally unoccupied band or conduction band in such a system. Even the casually abundant references to overlapping π orbitals should not conceal the absence of ionization states in the solids.

Exciton bands represent a more attractive concept. Multipole interactions can split the molecular energy levels into exciton bands. The Heitler-London concept recognizes the virtual electron localization that appears to be encountered in many of the systems to be mentioned. At the same time, it provides the possibility for eventual separation of positive and negative charges and will be seem to have various other features which are consistent with present information.

The thermoelectric coefficient $Q = \Delta v/\Delta T$ (in microvolts at 30°C.) is generally too much smaller than expected for a simple intrinsic elemental semiconductor. Indeed, a value observed for phthalocyanine of about 50 μv./°C. at room temperature suggests that the Fermi level lies below the edge of the valence band, rather than in the middle of the energy gap as might be conventionally expected.[9] In some cases, however, the thermoelectric coefficient apparently varies little with temperature, leading to a question of whether the population of charges really changed much with temperature. This would suggest that the principal temperature dependence of conductivity is actually that of mobility. In the condensed ring polymer systems discussed below, the Q coefficient did vary suggesting that an equilibrium population of carrier was indeed dependent on the temperature of the solid.

Electric Environment in Synthetic Polymer Solids

While many of the principles noted above seem to hold for relatively imperfect structures, such as types of organic molecular crystals, it must be emphasized that synthetic polymer solids are far less periodic in arrangement than any of the other systems so far considered. Indeed, they have a statistical disorder comparable to liquids, but nevertheless certain strong structural features do repeat, as characteristic "hopping" distances throughout the solid. It is also typical of many of the polymers studied that they form bonding continua of some sort throughout any specimen being studied. Thus, they rarely have the granular, compacted powder, qualities which do strongly emphasize surface effects. Nevertheless, some of these polymers during thermal conversion develop a certain porosity which can, of course, yield extremely large internal surface areas in any particular specimen. In summary, all the usual reservations about the problems of electrodes, continuity of the sample, of fluctuations in its purity and regularity of atomic arrangement, of effect of adsorbed gases, and so forth, must be considered.

Nevertheless, it has been possible to prepare a wide range of structural environments for studying conductivity related to the variety of bonding accessible to the carbon atom and to its derivatives with hydrogen, nitrogen, and oxygen.

In seeking overall relations of structure to properties, there are fortunately some examples of electrical activity in simple synthetic polymers whose configurations are comparatively well understood. Linear polyamides or nylons are particularly interesting examples. In Figure 1,

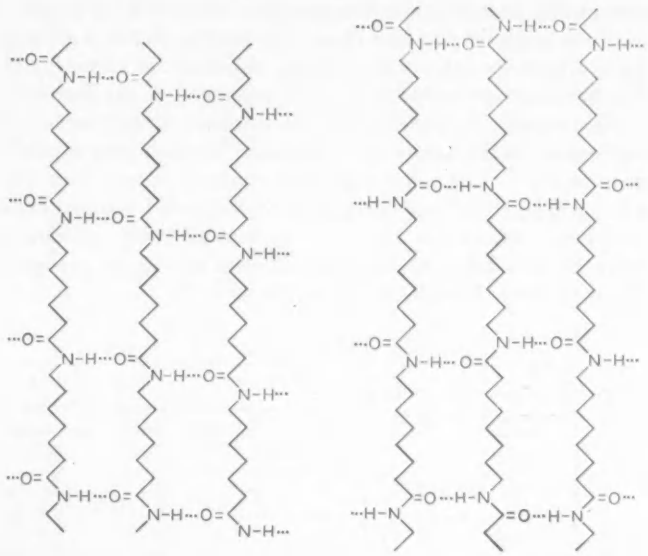


Fig. 1. Schematic diagrams of (*a*) solid structure of polyamide chains made from odd-numbered ω-amino acids or even-numbered di(amines and acids); (*b*) solid structure of polyamide chains made from even-numbered ω-amino acids or odd-numbered di-(amines and acids).

the packing of the polar groups and the association of the amide hydrogen, by strong polar influences, with the oxygen on neighboring chains is shown in rough schematic form. This association is somewhat different for odd- and even-member chains.[20,22] Recent studies have established in detail[2,18] the temperature-dependent generation and transport of charge carriers, which seem to include hydrogen ions moving along sheets of interacting intermolecular secondary bonds.

These effects, which are nicely reproducible, reflect an activation energy which varies comparatively little with changes in the detailed positions of the dipole layers diagrammed in Figure 1. A value of about 1.5 e.v. is probably determined more by the internal order and hence molecular motion of the system than by detailed variations in crystal structure.[20] This interesting sensitivity to the environment for a conduction process involving strong polarity or indeed having a possible exciton analogy in the detachment of a proton and electron from its bonding pair is nicely brought out by the d-c conductivity values related by McCall to a temperature t_1 of equivalent chain motion. In Table I, a series of polyamides are arranged in order of ascending concentration of amide groups per cubic centimeter. Immediately, the role of the amide hydrogen appears where *N*-methylation (replacement of the hydrogen) reduces the conductivity by about an order of magnitude from that of the unsubstituted 1010 polyamide.

The conductivity at equivalent temperatures then remains roughly constant until the marked structure change of the disordered terpolymer induces a rise of another order of magnitude. Both in this system and in the nylon 6 or ω-amino polyamide the placing of hydrogen-bonded groups is less specific than in the other structures. Thus, the terpolymer forms hydrogen-bonded layers in which there is much disorder and thus freedom to move.[22] The nylon 6 polymer contains at least two alternate crystal forms characteristic of both the even-numbered and the odd-numbered series as illustrated in Figure 1. It thus probably contains an exceptionally large number of its amide proton groups in configurations which favor transfer through the dipole planes.[23–25]

TABLE I[a]

Aliphatic polyamide according to number of C atoms in		Amide groups 10^{-21}/cm.³ (25°C	$\times 10^{11}$, σ at "equivalent" temperatures t_i, (ohm-cm.)$^{-1}$
Diamine	Acid		
10 (N–CH_3)	10	3.4	6
10	10	3.8	54
6	9	4.7	48
6	10	4.7	23
7	9	4.7	96
Terpolymer { 6	6	5.6	780
Terpolymer { —	6	5.6	780
Terpolymer { 6	10	5.6	780
— (ω-amino)	6	6.1	530
6	6	6.2	57

[a] Data of McCall.[19]

The detailed mechanism of charge transfer in these systems deserves continuing studying not only because of their similarity to the polypeptides, in chemical linkages, but also because the alternating current properties such as the dielectric constant, and the dielectric loss show striking increase at low frequencies (a few kilocycles) as the temperature is raised to provide activation of the charge carriers themselves.[2,18] Thus, when the conductivity of nylon 610 has risen to 2×10^{-8} ohm-cm. at 146°C., the dielectric constant, ϵ', is about 45 at 1 kcycle/sec. and the dielectric loss, ϵ'', is 27. The high polarization and accompanying charge mobility and/or charge population are associated with interchain spacings of about 5 A. Although we can say little at present of accompanying or associated electron excitation, various ionic states of the carbonyl groups and of their adjacent chain nitrogens can be involved. Typical behavior is shown in Figure 2.

There have already been practical uses of the effects of conductivity in polyamides, and of its large and uniform temperature coefficient. However, the general development of such effects in synthetic polymers is still barely beginning. One of the most interesting applications has been con-

trol of the total heat output of a network of resistance heating wires insulated with nylon from each other. As the temperature of the system rises, there is an automatic shunting of current through the resistance which then allows a temperature drop in the resistance elements themselves. Accordingly a kind of uniform regulation is imposed on the grid. Other extensively hydrogen-bonded systems such as cellulose, itself not

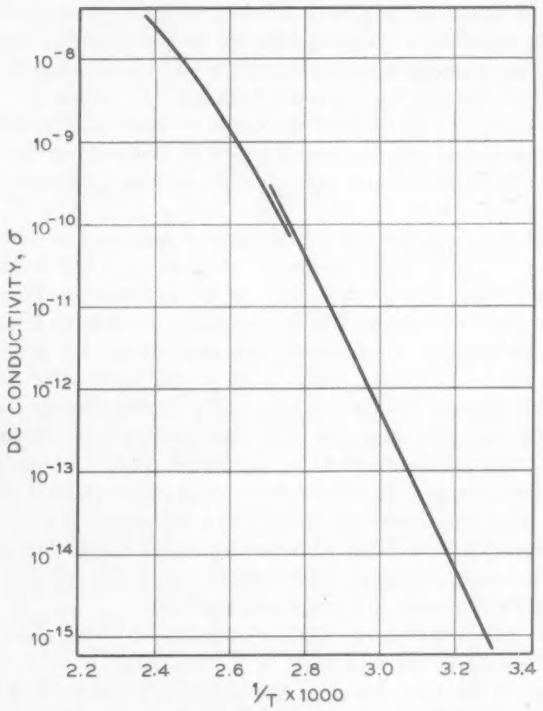


Fig. 2. Temperature dependence of the d-c conductivity σ of polyhexamethylene sebacamide.

a synthetic polymer, and polyvinyl alcohol also show appreciable conductivity as the temperature is elevated. However, the chemical stability in these cases is not so great as in the polyamides, and the effects are more obscured by impurities, varying moisture content, and so forth.

With this evidence of the possibilities of the effects of long-range charge transfer as a quality of the continuum in solid synthetic polymers, it is interesting to see whether systems could be prepared which would allow similar conduction of still other kinds of charges, such as holes and electrons.

Highly Conjugated Polymer Solids

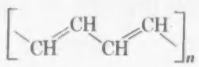
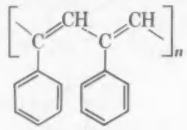
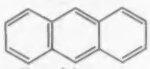
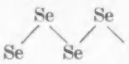
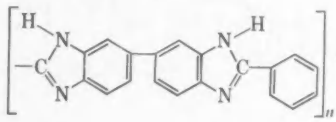
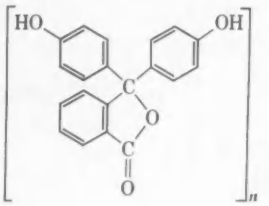
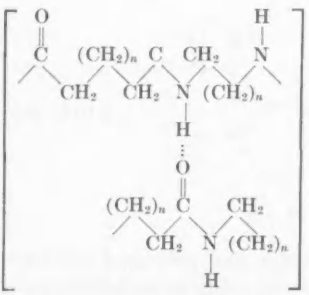
Indeed it has been found possible to prepare an essentially continuous series of carbon-bonded organic environments. These range between the highly insulating hydrocarbons such as polystyrene, with a specific resistance of about 10^{20} ohm-cm. to a carbon structure which nevertheless itself reflects in both atomic and superatomic qualities its insulating organic origins. The polymeric nature of these solids makes possible the simple application of electrodes and study of electromagnetic properties whereby one is able to trace the progression from the *sp*-bonding of aliphatic carbon through to the progressively overlapping π-orbitals of aromatic systems, which are in turn succeeded by radical states, then probably to polar excited states, and finally to the structure of pseudographites itself.[26,27] Many of these compounds are best prepared by thermal conversion of such polymers as polydivinyl- and polytrivinyl benzene, polyacetylenes, and polyacene-quinones.[8,38,44]

We should then consider this whole range of studies as occurring in various polymeric frameworks in which it is easy to vary the extent and nature of carbon bonding. In this sense, we do not know the detailed structure of any of these systems, but can estimate, or average from chemical analysis, spectroscopic observations, and electromagnetic properties, the over-all structures involved. Also, many x-ray scattering results have indicated the progress of ring condensation in these systems. Characteristically, the structure changes occur between about 200 and 700°C. Above this temperature of 700°C. the hydrogen content becomes less than one hydrogen atom per 50 or 60 carbons and high conductivity persists, as thermal conversion proceeds up to the temperatures of graphite formation. However, the crosslinks which are an essential aspect of many of the polymer conversions seem to inhibit graphitization indefinitely (at least through 2400°C.) in some of the systems studied.

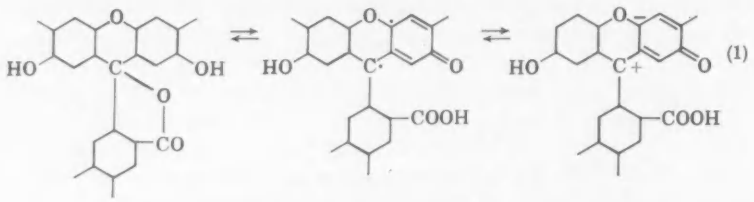
It is also found that a chemical conversion of hydrocarbons through oxidation facilitates the formation of a wide range of electronic states. Also recently it has been found by the extensive synthetic studies of Pohl and co-workers[33,35] that catalytic condensation, typically in the presence of zinc chloride, of aromatic compounds, linked with aromatic acid anhydrides yield what Pohl terms the polyacine quinone radical polymers (PAQR). These polymers are often made at temperatures between 250 and 350°C., where there also may be additional condensations yielding systems roughly analogous to the crosslinked hydrocarbon polymer structures when oxidized. The resulting systems, as noted in Table II, have room temperature resistivities of 10^4–10^6 ohm-cm., with typically low mobilities of 0.01–0.02 cm.^{2}/v.-sec.

The notable studies of Soviet scientists in this field have especially involved direct syntheses of highly conjugated systems such as polyacetylenes, polyphenyls, polydiethynyl benzenes and also various heteroatom polymers. Berlin and co-workers[36,37] have also reported on phenylene

TABLE II

	ρ, ohm–cm. (~25°C.)	E_A e.v.	Q, μv./°C.	spins/g.	Reference
	1×10^4 (cryst.) 10^9–10^{12} (amorphous)	0.9 1.6		10^{19}	52 37
	5×10^{10}	2.2–0.43		10^{17}–10^{19}	37
	10^{15}	0.80	1		3
Graphite (in C Planes)	5×10^{-5}				3
($\perp$ C Planes)	3				
Diamond IIb	10^2–10^3	~0.2	1200(p)		
	10^5–10^6	0.02	5–17		
	5×10^{12}	1.1		—	36,37
	1×10^8	0.64			33,34
	10^{15}	1.45		—	2,18
Anthraquinone pyromellitic anhydride (306°C.)	2×10^4	0.38	99(p)	2.4×10^{19}	33,34, 36,37
Polyphenylene aminoquinones		0.5		10^{21}–10^{23}	37

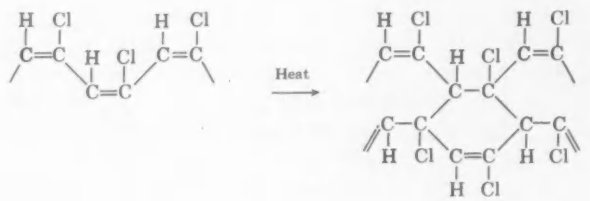
azo compounds, polyphenylene oxides, and condensation products which they call polyzanthines made from hydroquinone and pyromellitic anhydrides.[37,45] Evidently, the general configuration of this system is sterically and electrically analogous to some elements depicted in Figure 3. Such a reaction is represented in eq. (1).



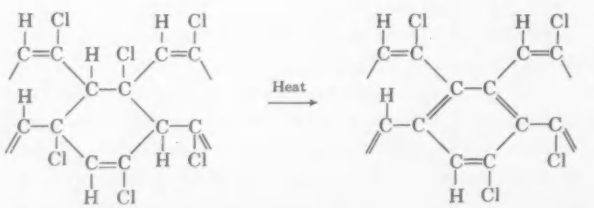
(1)

Finally, a third approach to the preparation of these structures is seen in the thermally abstracted polymers. Thus, polyvinylidene chloride on heating loses HCl progressively, and ultimately quantitatively to leave the condensed carbon residue behind,[28,31,43,46,47] as shown in eq. (2).

+3 HCl (2a)

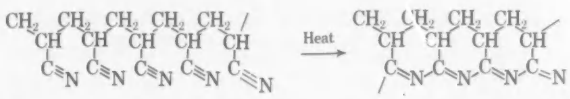


(2b)



+2 HCl (2c)

Other chain polymers such as polyvinyl chloride and polyvinyl alcohol[48] yield less simply derived unsaturates with considerably more carbon loss. Polyacrylonitrile is extensively converted to an electronically active and nonlinear system according to schemes like that shown in eq. (3).[38,41,44,49–51] Here, further dehydrogenation is almost certain.



Now the ideas to be derived from these diversities of original structures are that progressive bond redistribution into highly conjugated configurations universally results in important concentrations of electrons in a paramagnetic state. These unpaired spins reflect various kinds of excitations,

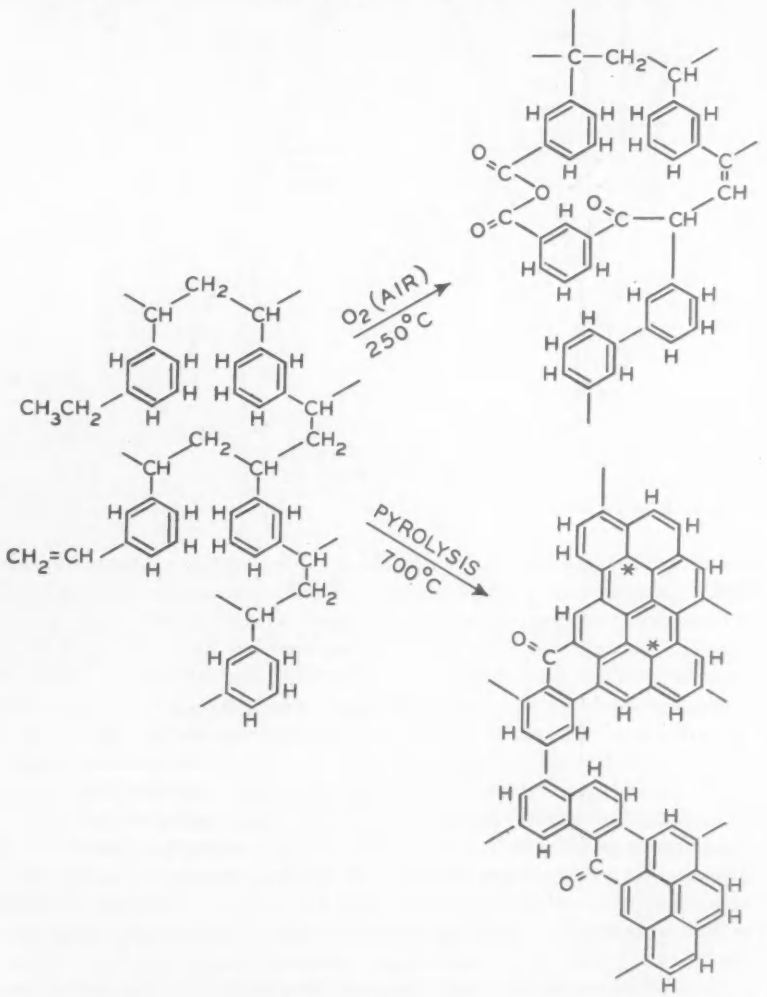


Fig. 3. Conversion of divinylbenzene/ethylvinylbenzene copolymer to electronically active derivatives.

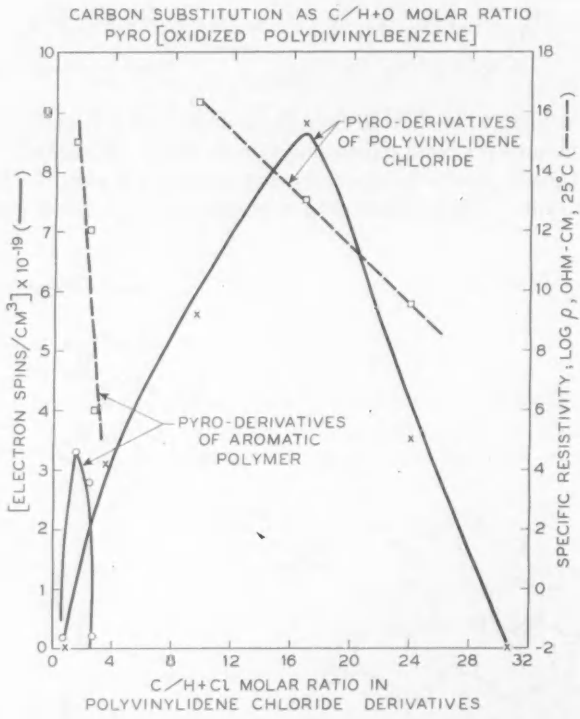

CARBON SUBSTITUTION AS C/H+O MOLAR RATIO
PYRO [OXIDIZED POLYDIVINYLBENZENE]
PYRO-DERIVATIVES OF POLYVINYLIDENE CHLORIDE
PYRO-DERIVATIVES OF AROMATIC POLYMER
[ELECTRON SPINS/CM³] x 10⁻¹⁹ (——)
SPECIFIC RESISTIVITY, LOG ρ, OHM-CM, 25°C (— — —)
C/H+Cl MOLAR RATIO IN POLYVINYLIDENE CHLORIDE DERIVATIVES

Fig. 4. Relation of free spin content to electronic conductivity of carbon networks.

whose detailed explanation remains one of the interesting challenges in this field. Generally, the concentrations of these free spins are estimated, from electron spin resonance absorption, to range from 10^{15} to 10^{19} per cubic centimeter. Second, it is found that the direct current conductivity of these systems increases particularly markedly when the structure is attained which represents the maximum free spin concentration for any particular preparation of the solid. (There seems to be some minor exceptions to this principle among the polyacene quinone radicals developed so largely by Pohl and collaborators. Here is found in some cases that the conductivity at 25°C. is actually higher than the values observed after treatment of the polymer at 400–600°C., but in the absence of special complications it appears that even in these systems, such as the polymer made from equimolar proportions of phenolphthalein and pyromellitic anhydride, the effect of heat is generally to produce a steep increase in room temperature conductivity.)

Thus, the general relation of the free spin content to electronic conductivity of carbon networks is illustrated in Figure 4. Here the electron free spin content as determined from electron paramagnetic resonance spec-

troscopy is scaled on the left-hand side of the figure whereas the logarithm of the specific resistivity at 25°C. is plotted on the right-hand side.

The large right-hand graphs are with reference to the substituents on carbon in a series of derivatives obtained by pyrolysis of polyvinylidene chloride. More compacted plots of the resistivity, also shown as a broken line, and the small dome-shaped curve, are from the thermal conversion of oxidized polydivinylbenzene networks. Many similar plots of specific representatives of the classes of polymers cited above could be inserted on

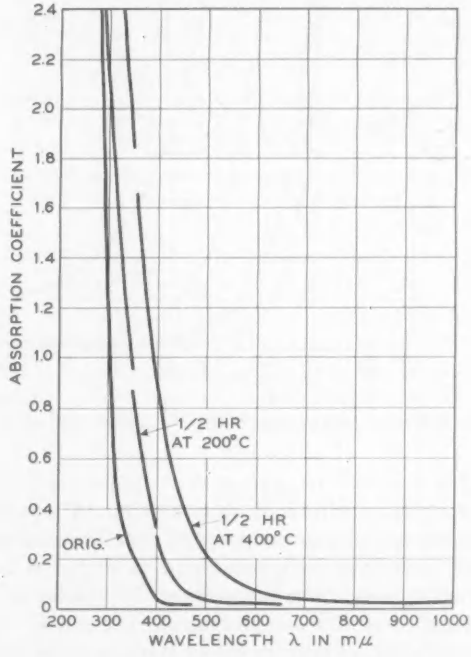


Fig. 5. Light absorption of divinylbenzene (~40%)/ethylvinylbenzene (~60%) copolymer film before and after heating in pure N_2.

such a diagram. Most would show a closely analogous behavior to one or the other of the rather extreme systems depicted. Thus, the right-hand curves for polyvinylidene chloride represent the structural alterations as linear carbon chain is progressively cyclized and converted to an extensive carbon network.

On the other hand, the polydivinylbenzene derivatives show an extremely extensive although isolated aromatic ring content in the first place. Apparently, vastly less alteration of primary carbon valences is necessary to produce electronic excitation into a paramagnetic condition, and eventually the extensive charge movement represented by the conduction.

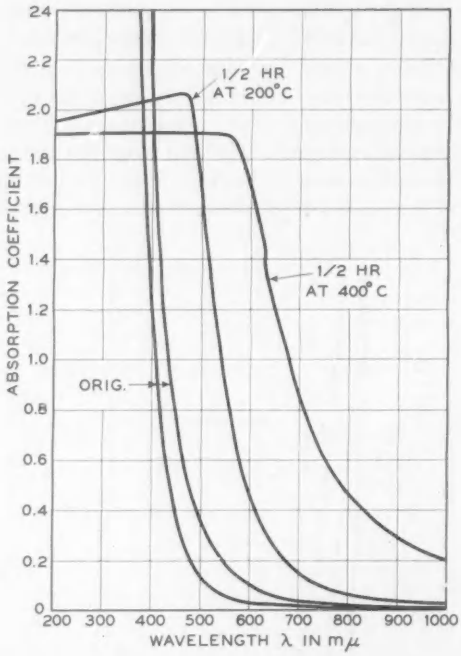


Fig. 6. Light absorption of polyvinylacetylene film before and after heating in pure N_2.

We shall seek presently to refer this behavior to general principles of conductivity in solids, but also we note that the classical organic structures involved reflect the well-known generation of radicals due to rigidity of the lattice of carbon atoms during the various thermochemical reactions involved. Thereby, radical recombination is prevented. These radicals can, of course, act electronically as donors and acceptors, depending on the circumstances of ionization or electron acquisition. Also we find that as the thermal conversion of the polymer proceeds, the optical absorption of the polymer structures is progressively shifted toward the red, as shown in Figure 5 for the polydivinylbenzene films and in Figure 6 for polyvinylacetylene films. In addition to effects from the remarkable population of unpaired spins there is also reflected a generalized mechanism for electronic excitation, as represented by the character of the optical absorption.

The diffuse x-ray scattering from these structures shows the continuously varying, liquid-like molecular packing characteristic, of aromatic hydrocarbons as they are transformed to a highly disordered, condensed ring structure. Values approach the typical 1.40 A. intraplanar atom spacings, and have *C*-spacings or interplanar distances of about 3.7 A.

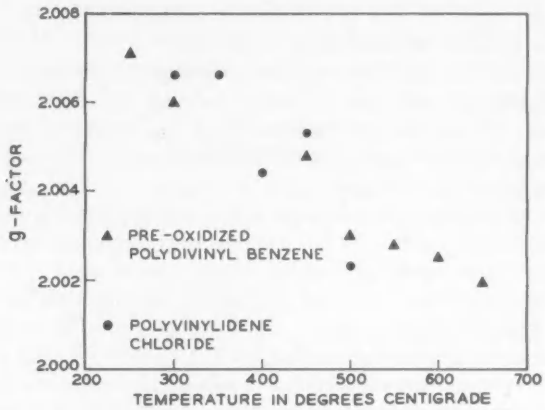


Fig. 7. g-Factor of preoxidized polyvinylbenzene and polyvinylidene chloride residues as a function of preparation temperature.

This is roughly 10% greater than the planar separations in graphite crystallite structure itself, and heating 8 hr. at 2400°C. causes only a modest reduction in the C-spacing. Distribution of intensity of scattered radiation shows a slight sharpening of (002) planar feature. However, this is still so broad that it is hardly resolved on the polymer scattering diagrams, even when most of the hydrogen has indeed been removed. Other high-order spacings characteristic of a true graphite net structure have not been observed.[27]

Having noted these trends in structure, we can now say that certain limiting properties will apply to elements of this structure. On the one hand, when it is behaving as a truly conjugated hydrocarbon, such as the polyenes as well as amorphous polyacetylenes, concentration of unpaired electron spins is reported to vary from about 5×10^{19} per gram for the highly crystalline product down to about 1×10^{18} for various amorphous structures.[52] The conductivity similarly runs from 1.4×10^{4} ohm-cm. resistance for the crystalline specimen containing the higher number of spins up to a resistance of 10^{9} or even 10^{12} ohm-cm. for certain of the amorphous specimens.[52] The chains involved appeared, from spectroscopic studies, to be fully extended, *trans*-conjugated double bond configurations. Except when there was an appreciable content of oxygen in the specimens, the characteristics of linear unsaturated conjugated chains are probably reasonably represented. The possible participation of such extensive conjugated system in photosynthetic energy transfers through carotene donor–acceptor complexes has already been remarked by Platt.[53] Then, since thermal conversion gives a method of still further conjugation and compaction of the carbon bonding, another extreme can be seen in the intensively studied behavior of impure graphites and electrical properties during graphitization itself. Another interesting structure having highly conjugated

regular chain configurations has recently been reported by W. P. Baker, Jr., from the isotactic polymerization of allylene.[54]

It appears that as polymer structures are progressively dehydrogenated, there is a significant portion of sterically fixed edge atoms left with unsatisfied valences. These can pull electrons from the interior of the aromatic ring system of the particular domain, and π-electrons may easily transfer to the thus vacated σ-orbitals. This, of course, will vary the nature of conduction as the thermal treatment varies the proportions of these different carrier influences.[55,56] These radicals thus frequently become bound negative ions which would leave mobile holes in the interior. It is interesting that the activation energy for conduction, arising from the processes related to this, decreases from 0.6 e.v. for a polyvinylidene chloride derivative with the empirical formula (C_5HCl) to 0.36 e.v. for a structure having an empirical formula of about ($C_{10}HCl$). Likewise, changing environment of electrons is shown by range of paramagnetic g-factors as seen in Fig. 7.

These conditions emphasize the key issue in the understanding of polymer conduction. This is how actual ionization finally is achieved in systems where the difference between ionization energy and electron affinity is almost always 4 or 5 e.v., and with the dielectric constant often little above 3. Special conditions for actual ion formation are subjects of a greatest interest at this stage in the investigation of organic conduction mechanisms. This indeed is also central in regard to the polyamide conduction processes discussed at the outset. While extensive and interesting speculation has been directed from many points of view to this issue, the role of exciton states is presently a most attractive hypothesis. Both Northrop and Simpson[14] and Riehl[57] in 1958 suggested interesting stepwise approaches to ionization through interaction with a series of molecular field conditions. This led Choi and Rice[58] to show a considerable probability of the transfer of excitation energy between two excited molecules with nonoverlapping electronic wave functions. They believe that in an organic crystal, such exciton–exciton interaction can lead easily to photoconductivity, and under the conditions we are considering could likewise be thermally induced. As they point out, this problem of exciton–exciton interaction will be subject to all sorts of imperfections, surface conditions, and impurities, but it does represent a kinetic system in which there is credible opportunity for charge generation in the complex, organic-bonded networks that we have discussed in the polymer classes. Indeed experiments of Silver and coworkers[59] on the photogeneration of carriers in anthracene seem to support strongly the proposals of the Choi-Rice theoretical suggestion. Obviously an extensive range of penetrating experiments now remains to be accomplished, on some of the better characterized or controlled conducting polymer structures. However, we demonstrated that there is wide convergence of behavior among systems nominally derived from highly different starting compounds. It seems likely that these types of organic polymer conductors will continue to yield important information on the whole sub-

ject of electronic environments. And this detailed behavior of electrons and other charge carriers under special bonding circumstances in other forms yields the wondrous diversity of organic chemistry and of the natural processes based upon it.

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Determination of Active Centers in Stereospecific Diene Polymerization

(*J. Polymer Sci.*, C4, 211–232, 1964)

by W. COOPER, D. E. EAVES, G. D. T. OWEN, and G. VAUGHAN

In the last column of Table II on page 217, the first six figures quoted for diisopropyl ether should be: 0.81, 1.06, 3.86, 2.90, 2.81, and 2.51.

On page 231, Dr. Vaughan's reply to Dr. Caunt's question in the discussion section contains several errors. A suitably corrected version follows.

G. Vaughan (*Dunlop Rubber Co., Ltd., Birmingham, England*): In our systems, experiments which show longer induction periods than normal also show corresponding changes in the numbers of C—Al bonds so that extrapolations still give positive values for the number of active centers. Since we have shown that all the polymer molecules are labelled we feel that the technique used is sound and not purely fortuitous. We have indicated in the paper that there are certain approximations made already so we are not claiming our propagation constants as being absolute. In answer to the second part, we take great care to remove the impurities from our starting materials so the possibility of the donor acting in this way is remote. There is the chance that certain retarders are generated in the system as indicated by Dr. Caunt, but as our measurements are made at low conversions the concentration of these compared with aluminum trialkyl will be very low. In addition, it is difficult to explain the large increases in the number of active sites in these systems by such a mechanism. At this stage, as indicated in the paper, we do not know how the donor functions in causing the large increases in rate reported in several papers.

Production of Polyoxymethylene of High Molecular Weight and High Crystallinity from Trioxane

(*J. Polymer Sci.*, C4, 953–965, 1964)

by M. BACCAREDDA, E. BUTTA, and P. GIUSTI

F. Morelli's name was omitted from list of authors in this paper.

Grafting of Styrene onto Teflon and Polyethylene by Preirradiation

(*J. Polymer Sci.*, **C4**, 1173–1193, 1964)

by J. DOBÓ, A. SOMOGYI, and T. CZVIKOSZKY

In Dr. Rossi's Discussion (pp. 1189–1193), two corrections are necessary.

The equation at the bottom of page 1191 should read:

$$R_T = \sqrt{\frac{K_1}{K_2}}\, I^A = \sqrt{\frac{K_1}{K_0}}\, I^A$$

The equation at the top of page 1192 should read:

$$A = \frac{e^{2T\sqrt{K_1 K_0 I}} - 1}{e^{2T\sqrt{K_1 K_0 I}} + 1}$$

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